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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US97/12383 <b>(22) International Filing Date:</b> 16 July 1997 (16.07.97)  <b>(30) Priority Data:</b> 9615630.2                      25 July 1996 (25.07.96)                      GB  <b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> MCKELVEY, Graham, Neil [GB/GB]; 37 Raglan Road, Knaphill, Woking, Surrey GU21 1AR (GB). YOUNG, Wendy, Victoria, Jane [GB/GB]; 70 Edgell Road, Staines, Middlesex TW18 2EX (GB).  <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> BR, CN, JP, MX, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> SHAMPOO COMPOSITIONS  <b>(57) Abstract</b> <p>A shampoo composition comprising: (a) from about 0.1 % to about 10 % by weight of short chain alkyl sulfate surfactant having a carbon chain length of 10 carbon atoms or less; (b) from about 0.1 % to about 10 % by weight of ethoxylated alcohol; and (c) from about 1 % to about 60 % by weight of auxiliary surfactant selected from anionic surfactant other than the short chain alkyl sulfate of (a), nonionic surfactant other than the ethoxylated alcohol of (b), amphoteric and cationic surfactants and mixtures thereof; (d) water. The shampoo compositions of the invention are valuable for the provision of improved rinsibility, excellent cleansing, and improved hair conditioning characteristics such as hair feel, hair shine, hair volume and manageability.</p>		

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## Shampoo Compositions

### Technical Field

The present invention relates to cleansing compositions suitable for cleansing the hair and/or skin containing a surfactant system, short chain alkyl sulfate and ethoxylated alcohol.

### Background of the Invention

Shampoo compositions should cleanse the hair and scalp and be safe to the user. In addition to the deterative surfactants for cleansing the hair, it is highly desirable for shampoos to contain additional ingredients such as conditioning agents, styling agents and dandruff control actives.

As well as removing sebum and dirt from the hair it is desirable that shampoo compositions should also cleanse residues of hair products, such as, gels, sprays etc. However, in combination with this need for effective cleansing, it is also desirable that the shampoo does not leave the hair feeling stripped of its natural conditioning oils. Further important parameters in the formulation of shampoo compositions are in-use characteristics such as lather volume, creaminess and rinse feel and after-use characteristics such as hair shine and hair volume. Thus, it would be desirable to develop an easily rinsed, lathering, conditioning shampoo for the delivery of improved hair cleaning and residue removal in combination with good hair shininess and volume characteristics.

Numerous approaches for improving hair cleansing, rinsibility, lather volume, lather quality, rinse feel, hair shine and hair volume have been suggested. For example, deterative surfactants, such as alkyl ethoxy sulfates can cleanse oily residues, such as sebum, from the hair; conditioning agents, such as silicone oils, can improve hair feel and appearance; suds boosters such as cocomoethanolamide, can improve lather volume and quality; cationic polymers, such as Varisoft (TN) or Luviquat (TN), can improve rinse feel, silicone oils, can improve hair

shine and styling agents, such as polymeric styling resins can improve hair volume.

However, some surfactants, in addition to cleansing the hair of oily soils, such as sebum, can deposit surfactant residues onto the hair. Thus, formulation of shampoo compositions requires balancing of the cleansing and conditioning ingredients used so that both effective cleansing, improved soil removal and good deposition of conditioning agents are provided without negative effects such as undesirable deposition of surfactant residues onto the hair.

Thus there is a continued desire to provide shampoos which can provide effective cleansing of the hair, good lather volume and quality attributes, and improved rinsibility from the hair. It is a further desire to provide shampoos which deliver improved conditioning attributes such as hair shine and hair volume. It is a still further desire to provide shampoos which deliver effective cleansing of the hair of oily soil and product residues and which are easily rinsed from the hair, yet do not strip the hair of natural oils, in combination with further improvements in hair shine and hair volume attributes.

Thus the objects of this invention are to provide shampoos in accordance with the above. It has now been found that the above effects can be obtained via the incorporation into shampoos of short chain alkyl sulfate and ethoxylated alcohol surfactants.

### Summary of the Invention

The present invention provides shampoo compositions comprising:

- (a) from about 0.1% to about 10% by weight of short chain alkyl sulfate surfactant having a carbon chain length of 10 carbon atoms or less.
- (b) from about 0.1% to about 10% by weight of ethoxylated alcohol; and

- (c) from about 1% to about 60% by weight of auxiliary surfactant selected from anionic surfactant other than the short chain alkyl sulfate of (a), nonionic surfactant other than the ethoxylated alcohol of (b), amphoteric and cationic surfactants and mixtures thereof;
- (d) water.

### Detailed Description of the Invention

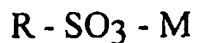
Shampoo compositions, as defined herein, include any composition comprising deterative surfactant or cleansing component which is capable of cleaning the hair and / or skin. The shampoo compositions of the present invention are especially useful for cleansing the hair and / or skin.

All concentrations and ratios herein are by weight of the cleansing composition, unless otherwise specified. Surfactant chain lengths are also on a weight average chain length basis, unless otherwise specified.

### Short Chain Alkyl Sulfate

As an essential feature the shampoo compositions according to the invention comprise a short chain alkyl sulfate surfactant. Short chain alkyl sulfate surfactants are valuable in the compositions of the invention, in combination with ethoxylated alcohol nonionic, for the provision of effective cleansing, improved product rinsing, a desirable lather profile, excellent conditioning attributes and enhanced removal of cationic and polymeric conditioning agents and surfactant residues from the hair.

Short chain alkyl sulfate surfactants suitable for inclusion in the compositions of the present invention have the general formula (I):



wherein R is straight or branched chain alkyl or alkenyl, preferably straight chain alkyl, generally having a lipophilic chain length of 10 carbon atoms or less and wherein M is selected from alkali metals, ammonium or other suitable monovalent cation or mixtures thereof.

It should be understood that the definition of any particular carbon chain length, say C<sub>10</sub>, may contain certain proportions of both higher and lower carbon chain lengths as a direct function of its synthesis. The level of such material can be controlled by modification of the process and the nature of the starting materials. Preferred for use herein are short chain alkyl sulfates wherein the short chain length alkyl sulfate, in which at least about 50% w/w of the total alkyl sulfate content is C<sub>10</sub> or less, highly preferred for use herein are short chain alkyl sulfates wherein at least about 50% by weight of the total alkyl sulfate content is between about C<sub>8</sub> and about C<sub>10</sub>, especially preferred for use herein are short chain alkyl sulfates wherein at least about 50% by weight of the total alkyl sulfate content is C<sub>10</sub> alkyl sulfate. While C<sub>10</sub> alkyl sulfate is the preferred surfactant in the compositions of the invention, mixtures of short chain alkyl sulfates may also be used. Especially preferred in the shampoo compositions herein is short chain alkyl sulfate material containing at least about 80% by weight of the C<sub>10</sub>, preferably at least about 90% C<sub>10</sub>, more preferably at least about 95% C<sub>10</sub> and especially at least about 97% C<sub>10</sub> alkyl sulfate. Suitable short chain alkyl sulfate materials are available from Albright and Wilson Ltd. under the trade name Empicol LC35 (TN).

The short chain alkyl sulfate surfactant is present in the shampoo compositions of the present invention at a level of from about 0.1% to about 10%, preferably from about 0.5% to about 8%, more preferably from about 1% to about 6%, most preferably from about 2% to about 4% by weight. Especially preferred are shampoo compositions wherein the level of short chain alkyl sulfate surfactant is at least about 0.5%, more preferably at least about 1% and most preferably at least about 2% by weight of the composition.



Highly preferred for use herein are shampoo compositions comprising alkyl sulphate surfactant with alcohol ethoxylate and auxiliary surfactant, wherein from about 0.1 % to about 10% by weight of the total composition comprises short chain alkyl sulphate having a chain length of C<sub>10</sub> or less, and wherein no more than about 4%, preferably no more than about 2%, more preferably no more than about 1%, most preferably no more than about 0.5% by weight of the total composition comprises alkyl sulphate having a chain length of greater than 10 carbon atoms.

### Ethoxylated Alcohols

Ethoxylated alcohol surfactants suitable for use herein include monohydric, dihydric and polyhydric alcohol mono- and poly-ethoxylates and / or alkylated derivatives thereof. Preferred for use herein are ethoxylated alcohol surfactants having the general formula (II):



wherein R<sub>1</sub> is C<sub>4</sub>-C<sub>31</sub> hydrocarbyl, preferably C<sub>6</sub>-C<sub>19</sub> hydrocarbyl, more preferably C<sub>7</sub>-C<sub>11</sub> hydrocarbyl, most preferably C<sub>9</sub>-C<sub>11</sub> hydrocarbyl, including natural or synthetic materials having straight-chain, branched chain alkyl and /or alkenyl configuration, R<sub>2</sub> is typically, hydrogen, C<sub>1</sub>-C<sub>8</sub> alkyl or hydroxyalkyl and x is an average value of ethoxylation ranging from 1 to about 20, preferably from about 3 to about 15, more preferably from about 5 to about 12, most preferably from about 7 to about 10. Other ethoxylates corresponding to the formula, such as those formed from one or more alcohols such as butanol, isobutanol, hexanol, octanol, decanol, dodecanol, tetradecanol, pentadecanol, octadecanol, eicosanol, docosanol, tetracosanol and triacontanol, are also suitable for use herein.

Exemplary alcohol ethoxylates for use herein are those wherein R<sub>2</sub> is hydrogen. Preferred for use herein are C<sub>9</sub> to C<sub>11</sub> alcohols having an average degree of ethoxylation of about 6 (available from Shell under the trade name Dobanol 91-6 (TN)) and C<sub>9</sub> to C<sub>11</sub> alcohols

having an average degree of ethoxylation of about 8 (available from Shell under the trade name Dobanol 91-8 (TN)).

While not wishing to be bound by theory it is believed that the mixture of ethoxylated alcohol surfactant and short chain alkyl sulfate surfactant, and, optionally, alkyl ethoxy sulfate surfactant, is valuable for the provision of effective cleansing, improved product rinsing, a desirable lather profile, excellent conditioning attributes and enhanced removal of cationic and polymeric conditioning agents and surfactant residues from the hair. The preferred level of ethoxylated alcohol in the shampoo compositions of the present invention is from about 0.1% to about 10%, preferably from about 0.5% to about 10%, more preferably from about 1% to about 8%, most preferably from about 2% to about 6% by weight.

Especially preferred for use herein is a mixture of alcohol ethoxylate and short chain alkyl sulfate surfactant wherein the weight ratio of short chain alkyl sulfate surfactant to alcohol ethoxylate surfactant is in the range of from about 10:1 to about 1:10, preferably from about 5:1 to about 1:5, more preferably from about 3:1 to about 1:3.

Thus, according to a further aspect of the present invention there is provided a shampoo composition comprising:

- (a) from about 0.1% to about 10% by weight of short chain alkyl sulfate surfactant having a carbon chain length of 10 carbon atoms or less.
- (b) from about 0.1% to about 10% by weight of ethoxylated alcohol; and
- (c) from about 1% to about 60% by weight of auxiliary surfactant selected from anionic surfactant other than the short chain alkyl sulfate of (a), nonionic surfactant other than the ethoxylated alcohol of (b), amphoteric and cationic surfactants and mixtures thereof;

(d) water.

wherein weight ratio of short chain alkyl sulfate to alcohol ethoxylate is in the range of from about 10:1 to about 1:10, preferably from about 5:1 to about 1:5, more preferably from about 3:1 to about 1:3.

#### Auxiliary Surfactant System

As a further essential feature, the shampoo compositions of the present invention comprise auxiliary surfactants. Auxiliary surfactants suitable for inclusion in compositions according to the present invention generally have a lipophilic chain length of from about 8 to about 22 carbon atoms and can be selected from anionic, nonionic, amphoteric and cationic surfactants and mixtures thereof. The total level of auxiliary surfactant is from about 1% to about 60%, preferably from about 2% to about 30%, more preferably from about 3% to about 25% and especially from about 5% to about 20% by weight.

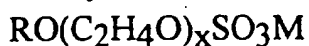
Preferably the shampoo compositions herein contain auxiliary deterative surfactants, more preferably water-soluble deterative auxiliary surfactants, although other surfactants may also be used. Especially preferred for use herein are auxiliary surfactants selected from anionic, nonionic and amphoteric surfactants other than short chain alkyl sulfate surfactants and ethoxylated alcohol surfactants as herein before described. Deterative surfactant, as defined herein, means, any surfactant having a lipophilic chain length of from about 12 carbon atoms and greater and which is capable of providing hair and / or skin cleansing attributes. Water-soluble surfactants, as defined herein, means a surfactant which is capable of forming a clear isotropic solution when dissolved in water at 0.2 % w/w under ambient conditions (about 20°C).

The level of the individual auxiliary anionic components, where present, is preferably in the range of from about 0.1% to about 20%, more preferably from about 0.1% to about 15%, and especially from about 2% to about 15% by weight of the composition, while the level of individual auxiliary amphoteric or nonionic components, where present, is in the range from about 0.1% to about 15% by weight, preferably from about 0.5% to about 10%, more preferably from about 1% to about 8% by weight.

Auxiliary anionic surfactants suitable for inclusion in the shampoo compositions of the invention include alkyl sulfates, other than the short chain chain alkyl sulfates as herein before described, ethoxylated alkyl sulfates, alkyl ethoxy carboxylates, alkyl glyceryl ether sulfonates, methyl acyl taurates, fatty acyl glycines, N-acyl glutamates, acyl isethionates, alkyl sulfosuccinates, alkyl ethoxysulphosuccinates, alpha-sulfonated fatty acids, their salts and/or their esters, alkyl phosphate esters, ethoxylated alkyl phosphate esters, acyl sarcosinates and fatty acid/protein condensates, and mixtures thereof. Alkyl and/or acyl chain lengths for these surfactants are C<sub>12</sub>-C<sub>22</sub>, preferably C<sub>12</sub>-C<sub>18</sub> more preferably C<sub>12</sub>-C<sub>14</sub>.

The shampoo compositions of the invention can comprise a total combined level of water-soluble auxiliary anionic surfactant at a level of from about 0.1% to about 30%, preferably from about 3% to about 25%, more preferably from about 5% to about 20% by weight.

Auxiliary anionic surfactants suitable for use in the shampoo compositions according to the present invention are the salts of sulfuric acid esters of the reaction product of 1 mole of a higher fatty alcohol and from about 1 to about 12 moles of ethylene oxide, with sodium, ammonium and magnesium being the preferred counterions. Alkyl ethoxy sulfate surfactants are valuable in shampoo compositions for the delivery of good lather volume attributes in addition to skin mildness attributes. Suitable alkyl ethoxy sulfates have the general formula (III):



wherein R is straight or branched chain alkyl or alkenyl, preferably straight chain alkyl, generally having a lipophilic chain length of from

about 8 to about 22 carbon atoms,  $x$  is the degree of ethoxylation and has an average value of from about 1 to about 12 and wherein  $M$  is selected from alkali metals, ammonium or other suitable monovalent cation or mixtures thereof. The cation  $M$  should be chosen such that the salt of the anionic surfactant is water-soluble. Solubility will depend upon the particular mixture of anionic surfactant and cations chosen.

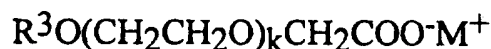
Preferred for use herein are alkyl ethoxy sulfate surfactants having a chain length in the range of from about 12 to about 22 carbon atoms and an average degree of ethoxylation of from about 1 to about 12, and mixtures thereof. Preferred also herein are the alkyl ethoxy sulfates having an average value of ethoxylation ( $x$ ) of from about 2 to about 6, preferably 2 to 4 moles of ethylene oxide, such as ammonium laureth-2 sulfate,  $\text{NH}_4^+$  laureth-3 sulfate and Na laureth-3 sulfate. In preferred embodiments, the anionic surfactant contains at least about 50% especially at least about 75% by weight of ethoxylated alkyl sulfate.

In addition to the broad range ethoxylated alkyl sulfates obtained via conventional sodium catalysed ethoxylation techniques and subsequent sulphation processes, ethoxylated alkyl sulfates obtained from narrow range ethoxylates (NREs) are also suitable water-soluble anionic surfactants for use in the present compositions. Preferred narrow range ethoxylated alkyl sulfates suitable for use herein are selected from sulfated alkyl ethoxylates containing on average from about 1 to about 6, preferably from about 2 to about 6, more preferably from about 3 to about 4 and especially about 3 moles of ethylene oxide, such as, NRE sodium laureth-3 sulfate. NRE materials suitable for use herein contain distributions of the desired ethylene oxide ( $\text{EO}_n$ ) in combination with both higher ethoxylates ( $\text{EO}_{n+1}$ ), ( $\text{EO}_{n+2}$ ), ( $\text{EO}_{n+3}$ ) and so on, and lower ethoxylates, ( $\text{EO}_{n-1}$ ), ( $\text{EO}_{n-2}$ ), ( $\text{EO}_{n-3}$ ) and so on. Preferred NRE materials for use herein contain an ethoxylate distribution such that the total amount of  $\text{EO}_n$ ,  $\text{EO}_{n+1}$  and  $\text{EO}_{n-1}$  is greater than the total amount of the other ethoxylates as well as non-ethoxylated material (i.e.,  $n = 0$ ) where present (calculated on a weight percent basis). NRE materials highly preferred for use herein contain distributions of the desired ethylene oxide ( $\text{EO}_n$ ) in the ranges of from

15% to about 45% by weight of  $\text{EO}_n$ , from about 10% to about 25% by weight of  $\text{EO}_{n+1}$  and from about 10% to about 25% by weight of  $\text{EO}_{n-1}$ . Highly preferred NRE materials contain less than about 9% by weight of ethoxylated alkyl sulfate having 7 or more moles of ethylene oxide and less than about 13% by weight of non-ethoxylated alkyl sulfate. Suitable laureth 3 sulfate NRE materials are available from Hoechst under the trade names GENAPOL ZRO (TN) Narrow Range and GENAPOL (TN) Narrow Range.

The shampoo compositions of the present invention may contain alkyl ethoxy carboxylate surfactant. Alkyl ethoxy carboxylate surfactant is valuable in shampoo compositions for the delivery of good rinsing performance and desirable lather characteristics.

Alkyl ethoxy carboxylates have the general formula (IV):



wherein  $\text{R}^3$  is a  $\text{C}_{10}$  to  $\text{C}_{15}$  alkyl or alkenyl group, preferably a  $\text{C}_{11}$ - $\text{C}_{15}$ , more preferably a  $\text{C}_{12}$ - $\text{C}_{14}$  alkyl or  $\text{C}_{12}$ - $\text{C}_{13}$  alkyl group,  $k$  is an average value of ethoxylation ranging from 2 to about 7, preferably from about 3 to about 6, more preferably from about 3.5 to about 5.5, especially from about 4 to about 5, most preferably from about 4 to about 4.5, and  $\text{M}$  is a water-solubilizing cation, preferably an alkali metal, alkaline earth metal, ammonium, lower alkanol ammonium, and mono-, di-, and tri-ethanol ammonium, more preferably sodium, potassium and ammonium, most preferably sodium and ammonium and mixtures thereof with magnesium and calcium ions.

Water-soluble anionic alkyl ethoxy carboxylate surfactants suitable for use herein are the  $\text{C}_{12}$  to  $\text{C}_{14}$  (average EO 3-6) ethoxy carboxylates and the  $\text{C}_{12}$  to  $\text{C}_{13}$  (average EO 3-6) ethoxy carboxylates. Suitable materials include salts of NEODOX 23-4 (TN) available from Shell Inc. (Houston, Texas, USA). Preferred for use herein are alkyl

ethoxy carboxylate surfactants wherein, when  $R^3$  is a  $C_{12}$ - $C_{14}$  or  $C_{12}$ - $C_{13}$  alkyl group and the average value of  $k$  is in the range of from about 3 to about 6, more preferably from about 3.5 to about 5.5, especially from about 4 to about 5 and most preferably from about 4 to about 4.5.

Preferred for use herein is a mixture of short chain alkyl sulfate and alkyl ethoxy sulfate anionic surfactants with ethoxylated alcohol nonionic surfactant wherein the short chain alkyl sulphate and alkyl ethoxy sulphate anionic surfactants are present at a total level of from about 0.1% to about 30%, preferably from about 1% to about 20%, especially from about 3% to about 15% by weight.

Especially preferred for use herein is a mixture of short chain  $C_{10}$  alkyl sulfate (available from Albright and Wilson Ltd. under the trade name Empicol LC 35 (TN)) and  $C_{12/14}AE_3S$  (available from Albright and Wilson Ltd. under the trade names Empicol AEB/T, AEC/T and AEC 70 (TN) and from Hoechst under the trade names Genapol ZRO narrow range (TN) and Genapol narrow range (TN)) wherein the weight ratio of short chain alkyl sulfate to alkyl ethoxy sulfate is in the range of from about 20:1 to about 1:20, preferably from about 10:1 to about 1:10, more preferably from about 5:1 to about 1:5, most preferably from about 3:1 to about 1:3.

Thus, according to a further aspect of the present invention there is provided a shampoo composition comprising;

- (a) from about 0.1% to about 10% by weight of short chain alkyl sulfate surfactant having a carbon chain length of 10 carbon atoms or less.
- (b) from about 0.1% to about 10% by weight of ethoxylated alcohol; and
- (c) from about 0.1% to about 20% by weight of ethoxylated alkyl sulfate surfactant;

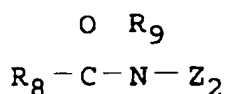
- (d) from about 1% to about 60% by weight of auxiliary surfactant selected from anionic surfactant other than the short chain alkyl sulfate of (a) and alkyl ethoxy sulfate of (c), nonionic surfactant other than the ethoxylated alcohol of (b), amphoteric and cationic surfactants and mixtures thereof; and
- (d) water.

wherein the ratio of short chain alkyl sulfate to alkyl ethoxy sulfate is in the range of from about 20:1 to about 1:20, preferably from about 10:1 to about 1:10, more preferably from about 5:1 to about 1:5, most preferably from about 3:1 to about 1:3.

The compositions of the present invention may also comprise auxiliary water-soluble nonionic surfactants other than the ethoxylated alcohol as herein before described. Exemplary auxiliary nonionic surfactants are selected from C<sub>12</sub>-C<sub>14</sub> fatty acid mono- and dialkanolamides such as cocoethanolamide, cocomonoisopropylamide and ethoxylated derivatives thereof, alkyl polysaccharides such as C<sub>10</sub>-C<sub>18</sub> alkyl polyglycosides and polyhydroxy fatty acid amide surfactants.

The auxiliary nonionic surfactant is preferably used in combination with other surfactants such as anionic and / or amphoteric. Auxiliary nonionic surfactant is generally used at levels of from about 0.1% to about 15%, preferably from about 0.1% to about 10%, more preferably from about 0.1% to about 8%, most preferably from about 0.5% to about 5% and especially from about 0.5% to about 2% by weight in the shampoo compositions of the present invention.

Polyhydroxy fatty acid amide surfactants suitable for use herein include those having the general formula (V).





The preferred N-alkyl, N-alkoxy or N-aryloxy, polyhydroxy fatty acid amide surfactants according to formula (V) are those in which  $R_8$  is  $C_5$ - $C_{31}$  hydrocarbyl, preferably  $C_6$ - $C_{19}$  hydrocarbyl, including straight-chain and branched chain alkyl and alkenyl, or mixtures thereof and  $R_9$  is typically, hydrogen,  $C_1$ - $C_8$  alkyl or hydroxyalkyl, preferably methyl, or a group of formula  $-R^1-O-R^2$  wherein  $R^1$  is  $C_2$ - $C_8$  hydrocarbyl including straight-chain, branched-chain and cyclic (including aryl), and is preferably  $C_2$ - $C_4$  alkylene,  $R^2$  is  $C_1$ - $C_8$  straight-chain, branched-chain and cyclic hydrocarbyl including aryl and oxyhydrocarbyl, and is preferably  $C_1$ - $C_4$  alkyl, especially methyl, or phenyl.  $Z_2$  is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof.  $Z_2$  preferably will be derived from a reducing sugar in a reductive amination reaction, most preferably  $Z_2$  is a glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilised as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for  $Z_2$ . It should be understood that it is by no means intended to exclude other suitable raw materials.  $Z_2$  preferably will be selected from the group consisting of  $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$ ,  $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{H}$ ,  $\text{CH}_2(\text{CHOH})_2(\text{CHOR}')\text{CHOH}-\text{CH}_2\text{OH}$ , where  $n$  is an integer from 1 to 5, inclusive, and  $R'$  is H or a cyclic mono- or poly-saccharide, and alkoxylated derivatives thereof. As noted, most preferred are glycityls wherein  $n$  is 4, particularly  $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$ .

The most preferred polyhydroxy fatty acid amide has the formula  $R_8(\text{CO})\text{N}(\text{CH}_3)\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}$  wherein  $R_8$  is a  $C_6$ - $C_{19}$  straight chain alkyl or alkenyl group. In compounds of the above formula,  $R_8\text{-CO-N}<$  can be, for example, cocoamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmiamide, tallowamide, etc.

A preferred process for making the above compounds having formula (V) comprises reacting a fatty acid triglyceride with an N-substituted polyhydroxy amine in the substantial absence of lower (C<sub>1</sub>-C<sub>4</sub>) alcoholic solvent, but preferably with an alkoxylated alcohol or alkoxylated alkyl phenol such as NEODOL and using an alkoxide catalyst at temperatures of from about 50°C to about 140°C to provide high yields (90-98%) of the desired products. Suitable processes for making the desired polyhydroxy fatty acid amide compounds are outlined in US-A-5,194,639 and US-A-5,380,891.

It should be recognised that along with the polyhydroxy fatty acid amides, the processes used to form them can also typically produce quantities of nonvolatile by products such as esteramides and cyclic polyhydroxy fatty acid amide. The level of these by-products will vary depending upon the particular reactants and process conditions. The suitable processes referred to above are advantageous in that they can yield rather low levels of by-products, including such cyclic amide by-product.

The polyhydroxy fatty acid amide surfactants suitable for use herein offer the additional advantages to the shampoo formulator that they can be prepared wholly or primarily from natural, renewable, non petrochemical feed stocks and are degradable. They also exhibit low toxicity to aquatic life.

Additional nonionic surfactants suitable for use herein include: long chain tertiary amine oxides corresponding to the following general formula:



wherein R<sub>1</sub> contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and R<sub>2</sub> and R<sub>3</sub> contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals. the arrow in the formula is a conventional

representation of a semipolar bond; Long chain tertiary phosphine oxides corresponding to the following general formula:

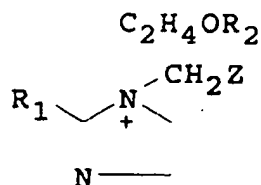


wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and R' and R'' are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety.

The compositions for use herein may also contain a water-soluble amphoteric surfactant at a level of from about 0.1% to about 15% by weight, preferably from about 0.5% to about 10%, more preferably from about 1% to about 8%, most preferably from about 1% to about 5% by weight.

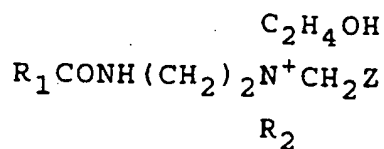
Amphoteric surfactants suitable for use herein include zwitterionics, such as betaines, amido betaines and sultaines, as well as:

(a) imidazolinium surfactants of formula (VI)



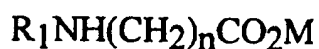
wherein R<sub>1</sub> is C<sub>7</sub>-C<sub>22</sub> alkyl or alkenyl, R<sub>2</sub> is hydrogen or CH<sub>2</sub>Z, each Z is independently CO<sub>2</sub>M or CH<sub>2</sub>CO<sub>2</sub>M, and M is H, alkali metal, alkaline earth metal, ammonium or

alkanolammonium; and/or ammonium derivatives of formula (VII)

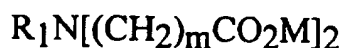


wherein R<sub>1</sub>, R<sub>2</sub> and Z are as defined above;

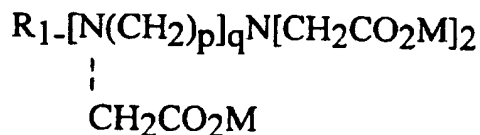
(b) aminoalkanoates of formula (VIII)



iminodialkanoates of formula (IX)



and iminopolyalkanoates of formula (X)



wherein n, m, p, and q are numbers from 1 to 4, and R<sub>1</sub> and M are independently selected from the groups specified above; and

(c) mixtures thereof.

Suitable amphoteric surfactants of type (a) are marketed under the trade name Miranol and Empigen and are understood to comprise a complex mixture of species. Traditionally, the Miranols have been described as having the general formula VI, although the CTFA Cosmetic Ingredient Dictionary, 3rd Edition indicates the non-cyclic structure V while the 4th Edition indicates yet another structural isomer in which R<sub>2</sub> is O-linked rather than N-linked. In practice, a complex mixture of cyclic and non-cyclic species is likely to exist and both

definitions are given here for sake of completeness. Preferred for use herein, however, are the non-cyclic species.

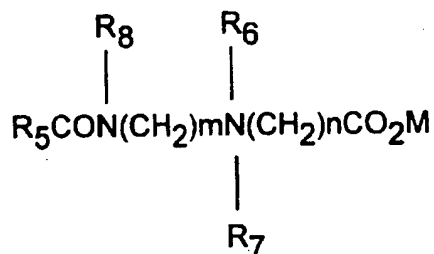
Examples of suitable amphoteric surfactants of type (a) include compounds of formula VI and/or VII in which  $R_1$  is  $C_8H_{17}$  (especially iso-capryl),  $C_9H_{19}$  and  $C_{11}H_{23}$  alkyl. Especially preferred are the compounds in which  $R_1$  is  $C_9H_{19}$ , Z is  $CO_2M$  and  $R_2$  is H; the compounds in which  $R_1$  is  $C_{11}H_{23}$ , Z is  $CO_2M$  and  $R_2$  is  $CH_2CO_2M$ ; and the compounds in which  $R_1$  is  $C_{11}H_{23}$ , Z is  $CO_2M$  and  $R_2$  is H.

In CTFA nomenclature, materials suitable for use in the present invention include cocoamphocarboxypropionate, cocoamphocarboxy propionic acid, and especially cocoamphoacetate and cocoamphodiacetate (otherwise referred to as cocoamphocarboxyglycinate). Specific commercial products include those sold under the trade names of Ampholak 7TX (TN)(sodium carboxy methyl tallow polypropyl amine), Empigen CDL60 (TN) and CDR 60 (TN) (Albright & Wilson), Miranol H2M Conc. (TN), Miranol C2M Conc. N.P.(TN), Miranol C2M Conc. O.P.(TN), Miranol C2M SF (TN), Miranol CM Special (TN) (Rhône-Poulenc); Alkateric 2CIB (TN) (Alkaril Chemicals); Amphoterge W-2 (TN)(Lonza, Inc.); Monateric CDX-38 (TN), Monateric CSH-32 (TN) (Mona Industries); Rewoteric AM-2C (TN) (Rewo Chemical Group); and Schercotic MS-2 (TN) (Scher Chemicals).

It will be understood that a number of commercially-available amphoteric surfactants of this type are manufactured and sold in the form of electroneutral complexes with, for example, hydroxide counterions or with anionic sulfate or sulfonate surfactants, especially those of the sulfated  $C_8$ - $C_{18}$  alcohol,  $C_8$ - $C_{18}$  ethoxylated alcohol or  $C_8$ - $C_{18}$  acyl glyceride types. Preferred from the viewpoint of mildness and product stability, however, are compositions which are essentially free of (non-ethoxylated) sulfated alcohol surfactants. Note also that the concentrations and weight ratios of the amphoteric surfactants are based herein on the uncomplexed forms of the surfactants, any anionic surfactant counterions being considered as part of the overall anionic surfactant component content.

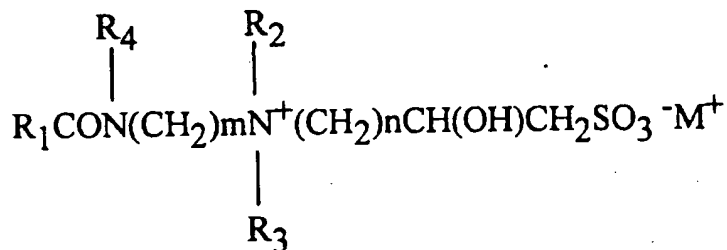
Examples of preferred amphoteric surfactants of type (b) include N-alkyl polytrimethylene poly-, carboxymethylamines sold under the trade names Ampholak X07 (TN) and Ampholak 7CX (TN) by Berol Nobel and also salts, especially the triethanolammonium salts and salts of N-lauryl-beta-amino propionic acid and N-lauryl-imino-dipropionic acid. Such materials are sold under the trade name Deriphat (TN) by Henkel and Miritaine (TN) by Rhône-Poulenc.

Betaine surfactants suitable for use herein include alkyl betaines of the formula  $R_5R_6R_7N^+(CH_2)_nCO_2M$  and amido betaines of the formula (XI):



wherein  $R_5$  is  $C_{11}$ - $C_{22}$  alkyl or alkenyl,  $R_6$  and  $R_7$  are independently  $C_1$ - $C_3$  alkyl,  $R_8$  is hydrogen or methyl,  $M$  is hydrogen, alkali metal, alkaline earth metal, ammonium or alkanolammonium, and  $n$ ,  $m$  are each numbers from 1 to 4. Preferred betaines include cocoamidopropyl dimethylcarboxymethyl betaine and , laurylamidopropyl dimethyl carboxymethyl betaine.

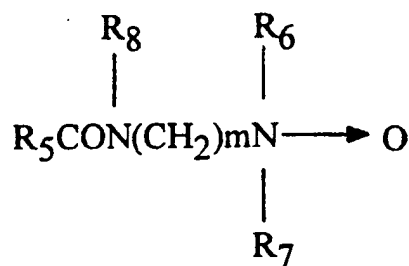
Water-soluble sultaine surfactants suitable for inclusion in the compositions of the present invention include alkylamido sultaines of the formula:



wherein  $R_1$  is  $C_7$  to  $C_{22}$  alkyl or alkenyl,  $R_2$  and  $R_3$  are independently  $C_1$  to  $C_3$  alkyl,  $R_4$  is hydrogen or methyl,  $M$  is H, alkali metal, alkaline

earth metal, ammonium or alkanolammonium and m and n are numbers from 1 to 4. Preferred for use herein is coco amido propylhydroxy sultaine.

Water-soluble amine oxide surfactants suitable for inclusion in the compositions of the present invention include alkyl amine oxide  $R_5R_6R_7NO$  and amido amine oxides of the formula:



wherein  $R_5$  is  $C_{11}$  to  $C_{22}$  alkyl or alkenyl,  $R_6$  and  $R_7$  are independently  $C_1$  to  $C_3$  alkyl,  $R_8$  is hydrogen or methyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium and m is a number from 1 to 4. Preferred amine oxides include cocoamidopropylamine oxide, lauryl dimethyl amine oxide and myristyl dimethyl amine oxide.

Cationic surfactants suitable for use herein include quaternary ammonium surfactants selected from mono  $C_8$  -  $C_{16}$ , preferably  $C_{10}$  -  $C_{14}$  N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl hydroxy ethyl or hydroxy propyl groups. Exemplary cationic surfactants for use herein include: di hydrogenated tallowamidoethyl hydroxyethylammonium methosulfate, available under the trade name Varisoft CB110 (TN) from Witco. It should be understood that cationic quaternary ammonium surfactants can act as conditioning cosmetic agents in the compositions herein.

Especially preferred for use herein are shampoo compositions comprising a mixture short chain alkyl sulfate surfactant and alkyl ethoxy sulfate surfactant with ethoxylated alcohol nonionic surfactant and amphoteric surfactant, wherein the weight ratio of ethoxylated alcohol to total anionic surfactant is in the range of from about 1:20 to

about 20:1, preferably from about 1:10 to about 10:1, more preferably from about 1:5 to about 5:1, most preferably from about 1:2 to about 2:1 and, wherein the weight ratio of ethoxylated alcohol nonionic surfactant to amphoteric surfactant is in the range of from about 5:1 to about 1:5, preferably from about 3:1 to about 1:3, more preferably from about 1:2 to about 2:1.

The above compositions are especially valuable for the provision of effective cleansing, improved product rinsing, a desirable lather profile, excellent conditioning attributes and enhanced removal of cationic and polymeric conditioning agents and surfactant residues from the hair as well as improved mildness to the skin of the user.

Thus according to a further aspect of the present invention there is provided a shampoo composition comprising:

- (a) from about 0.1% to about 10% by weight of short chain alkyl sulfate surfactant having a carbon chain length of 10 carbon atoms or less.
- (b) from about 0.1% to about 10% by weight of ethoxylated alcohol;
- (c) from about 1% to about 60% by weight of auxiliary surfactant selected from anionic surfactant other than the short chain alkyl sulfate of (a), nonionic surfactant other than the ethoxylated alcohol of (b), amphoteric and cationic surfactants and mixtures thereof; and
- (d) water.

wherein the weight ratio of ethoxylated alcohol to total anionic surfactant is in the range of from about 1:20 to about 20:1, preferably from about 1:10 to about 10:1, more preferably from about 1:5 to about 5:1, most preferably from about 1:2 to about 2:1 and wherein the weight ratio of ethoxylated alcohol nonionic



surfactant to amphoteric surfactant is in the range of from about 5:1 to about 1:5, preferably from about 3:1 to about 1:3, more preferably from about 1:2 to about 2:1.

In a highly preferred embodiment the composition comprises short chain alkyl sulphate surfactant and auxiliary anionic surfactant, such as alkyl ethoxy sulphate in combination with ethoxylated alcohol wherein, the weight ratio of ethoxylated alcohol nonionic surfactant to auxiliary anionic surfactant is in the range of from about 1:20 to about 4:1, preferably from about 1:10 to about 3:1, more preferably from about 1:5 to about 2:1.

#### Cosmetic Agent and / or Pharmaceutical active

As an additional optional feature the shampoo compositions according to the present invention may comprise a cosmetic agent and / or a pharmaceutical active, preferably at a level of from about 0.001% to about 10%, more preferably from about 0.01% to about 5%, most preferably from about 0.1% to about 3% and especially from about 0.1% to about 2% by weight.

Cosmetic agents suitable for use herein are defined as any agent which is capable of improving the appearance and / or feel of the hair and / or skin. Cosmetic agents preferred for use herein provide improvements in hair and / or skin feel and / or appearance via deposition onto the hair and / or skin. Cosmetic agents suitable for use herein include; conditioning agents, such as polyquaternium 10, polyquaternium 16, hydroxypropyl guar, and hydroxy propyl triammonium chloride; styling agents, such as poly vinyl pyrrolidone, poly vinyl pyrrolidone vinyl acetate, vinyl acetate / crotonic acid, vinyl acetate / vinyl butyl benzoate crotonic acid, octyl acrylamide acrylates / butyl aminoethyl methacrylate, polyquaternium 11, polyvinylpyrrolidone dimethyl ethyl methacrylate, vinyl carprolactam / poly vinyl pyrrolidone / dimethyl amino ethyl methacrylate, polyquaternium 4, sodium polystyrene sulfonate, vinyl acrylate / crotonate / vinyl neodecanoate copolymer; and, hair moisturising agents, such as, methyl gluceth-10, D-panthenol, PEG-6 capric /

caprylic glycerides, glycerine, wheat protein hydrolysate, tocopherol acetate.

### Conditioning Agent

Conditioning agents, as defined herein, are fundamental ingredients which can improve the appearance and / or feel of the hair and / or skin. Preferably conditioning agents for use herein should deposit onto the hair and /or skin for the provision of conditioning attributes both during and after-use of the shampoo compositions of the invention.

Conditioning agents suitable for use herein are selected from silicone materials, fatty alcohols, polymeric resins, polyol carboxylic acid esters, cationic polymers, insoluble oils and oil derived materials and mixtures thereof.

### Silicone Materials

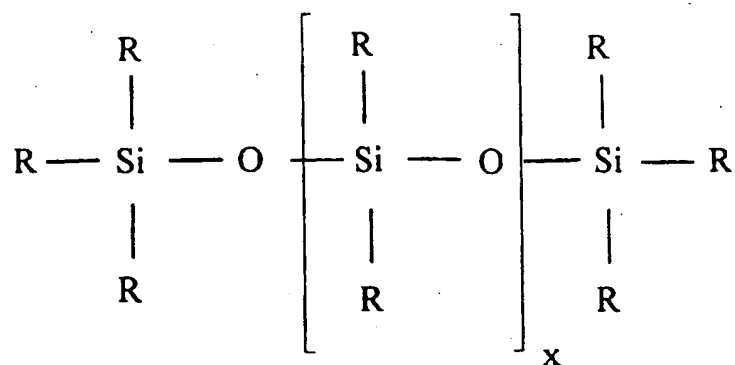
Suitable silicone conditioning agents for use herein are nonvolatile and insoluble in the shampoo composition and will intermix in the shampoo composition so as to be in the form of an emulsion, i.e., a separate, discontinuous phase of dispersed, insoluble droplets. These droplets are suspended with a suspending agent, numerous, non-exclusive suitable examples of which are described below. This dispersed silicone conditioning component will comprise a silicone fluid hair conditioning agent such as a silicone fluid and can also comprise other ingredients, such as a silicone resin to enhance silicone fluid deposition efficiency or, for example, enhance glossiness of the hair (especially when high refractive index (e.g. above about 1.46) silicone conditioning agents are used (e.g. highly phenylated silicones).

The silicone conditioning agent phase may comprise volatile silicone components. Typically, if volatile silicones are present, it will be incidental to their use as a solvent or carrier for commercially available forms of nonvolatile silicone materials ingredients, such as silicone gums and resins.

The silicone conditioning agent component for use herein will preferably have viscosity of from about 20 to about 2,000,000 centistokes at 25°C, more preferably from about 1,000 to about 1,800,000, even more preferably from about 50,000 to about 1,500,000, most preferably from about 100,000 to about 1,500,000.. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970.

The silicone conditioning agent component will generally be used in the shampoo compositions hereof at levels of from about 0.05% to about 10% by weight of the composition, preferably from about 0.1% to about 8%, more preferably from about 0.1% to about 5%, most preferably from about 0.1% to about 3%. The minimum level that is used in a particular composition should be effective to provide a conditioning benefit. The maximum level that can be used is not limited by theory, but rather by practicality. It is generally unnecessary and expensive to use levels in excess of about 8%, although higher levels can be used if desired.

One type of silicone fluid that can be used herein is a silicone oil. The term "silicone oil" shall mean flowable silicone materials having a viscosity of less than 1,000,000 centistokes at 25°C. Generally, the viscosity of the fluid will be between about 5 and 1,000,000 centistokes at 25°C, preferably between about 10 and about 100,000. Suitable silicone oils include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other insoluble, nonvolatile silicone fluids having hair conditioning properties can also be used. More particularly silicone oils hereof include polyalkyl or polyaryl siloxanes having the general formula (XII):



wherein R is aliphatic, preferably alkyl or alkenyl, or aryl, R can be substituted or unsubstituted, and x is an integer from 1 to about 8,000. Suitable unsubstituted R groups include alkoxy, aryloxy, alkaryl, arylalkyl, arylalkenyl, alkamino, and ether-substituted, hydroxyl-substituted, and halogen-substituted aliphatic and aryl groups. Suitable R groups also include cationic amines and quaternary ammonium groups.

The aliphatic or aryl groups substituted on the siloxane chain may have any structure as long as the resulting silicones remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair and / or skin, are compatible with the other components of the composition, are chemically stable under normal use and storage conditions, are insoluble in the composition, and are capable of being deposited on and, of conditioning, the hair and / or skin. The two R groups on the silicon atom of each monomeric silicone unit may represent the same group or different groups. Preferably, the two R groups represent the same group.

Preferred alkyl and alkenyl substituents are C<sub>1</sub>-C<sub>5</sub> alkyls and alkenyls, more preferably from C<sub>1</sub>-C<sub>4</sub>, most preferably from C<sub>1</sub>-C<sub>2</sub>. The aliphatic portions of other alkyl-, alkenyl-, or alkynyl-containing groups (such as alkoxy, alkaryl, and alkamino) can be straight or branched chains and preferably have from one to five carbon atoms, more preferably from one to four carbon atoms, even more preferably from one to three carbon atoms, most preferably from one to two carbon atoms. As discussed above, the R substituents hereof can also contain

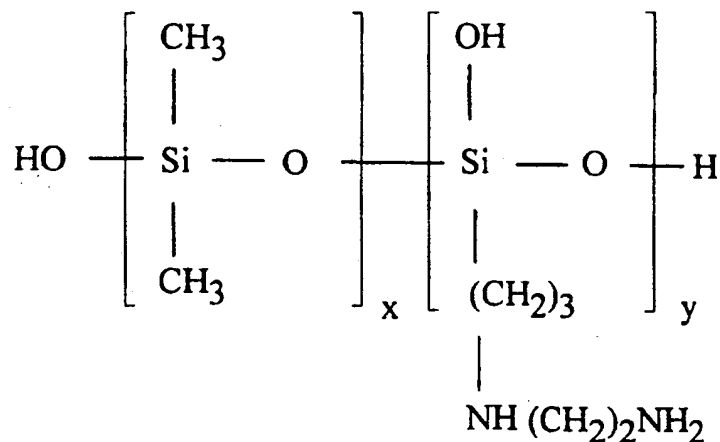
amino functionalities, e.g. alkamino groups, which can be primary, secondary or tertiary amines or quaternary ammonium. These include mono-, di- and tri- alkylamino and alkoxyamino groups wherein the aliphatic portion chain length is preferably as described above. The R substituents can also be substituted with other groups, such as halogens (e.g. chloride, fluoride, and bromide), halogenated aliphatic or aryl groups, and hydroxy (e.g. hydroxy substituted aliphatic groups). Suitable halogenated R groups could include, for example, tri-halogenated (preferably fluoro) alkyl groups such as  $-R^1-C(F)_3$ , wherein  $R^1$  is  $C_1-C_3$  alkyl. Examples of such polysiloxanes include polymethyl -3,3,3 trifluoropropylsiloxane.

The nonvolatile polyalkylsiloxane fluids that may be used include, for example, polydimethylsiloxanes. These siloxanes are available, for example, from the General Electric Company in their Viscasil R and SF 96 series, and from Dow Corning in their Dow Corning 200 series. Also suitable for use herein is Dow Corning DC 1664 (TN) 60,000 cstk polydimethyl siloxane with 300nm particle size which is preferably used in combination with a cationic polymer. Polydimethyl silicone is also known as dimethicone oil. Other suitable R groups include methyl, methoxy, ethoxy, propoxy, and aryloxy. The three R groups on the end caps of the silicone may also represent the same or different groups. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicones are polydimethyl siloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane is especially preferred.

The polyalkylaryl siloxane fluids that may be used, also include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

The polyether siloxane copolymers that may be used include, for example, a polypropylene oxide modified polydimethylsiloxane (e.g., Dow Corning DC-1248) although ethylene oxide or mixtures of ethylene oxide and propylene oxide may also be used. The ethylene

oxide and polypropylene oxide level must be sufficiently low to prevent solubility in water and the composition hereof. Alkylamino substituted silicones that can be used herein include those of the formula :

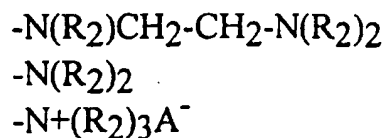


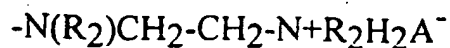
in which x and y are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

Cationic silicone fluids which can be used in the present compositions include those that correspond to the formula:



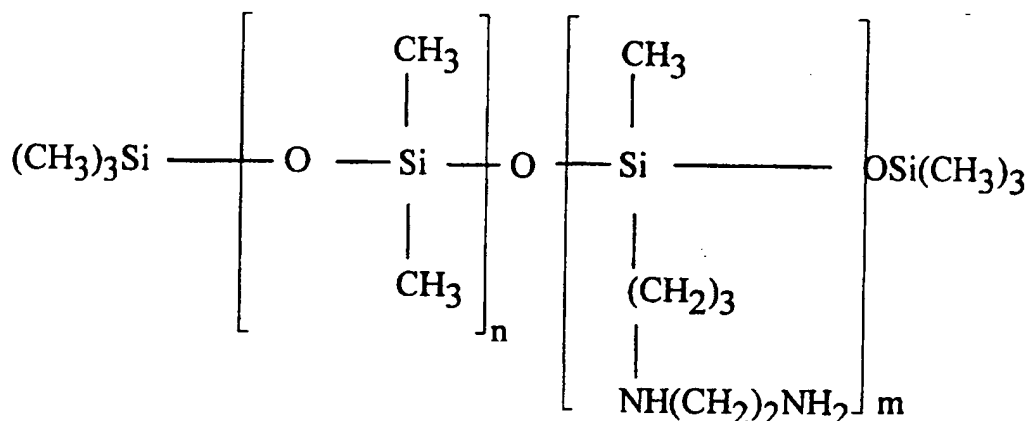
in which G is chosen from the group consisting of hydrogen, phenyl, OH, C<sub>1</sub>-C<sub>8</sub> alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R<sub>1</sub> is a monovalent radical of formula C<sub>q</sub>H<sub>2q</sub>L in which q is an integer from 2 to 8 and L is chosen from the groups:



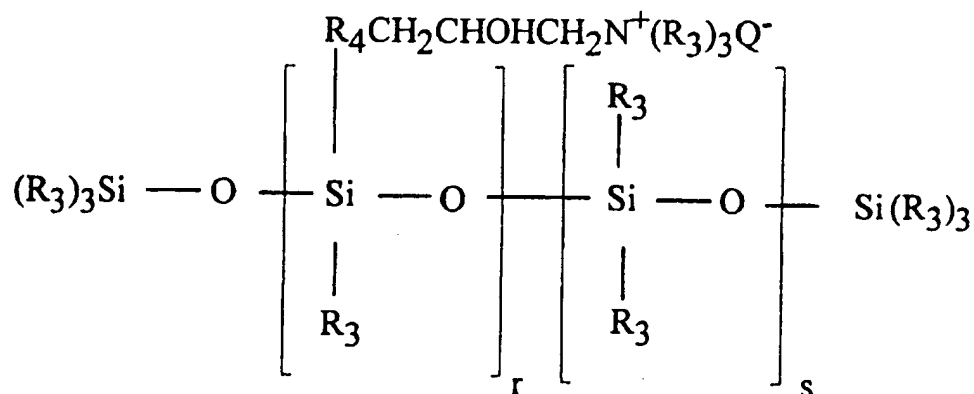


in which  $R_2$  is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and  $A^-$  denotes a halide ion.

An especially preferred cationic silicone corresponding to formula immediately above is the polymer known as "trimethylsilylamodimethicone", of formula:



Other silicone cationic polymers which can be used in the present compositions correspond to the formula:



in which  $R_3$  denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, and more especially an alkyl or alkenyl radical such as methyl;  $R_4$  denotes a hydrocarbon radical such as, preferably a  $C_1$ - $C_{18}$  alkylene radical or a  $C_1$ - $C_{18}$ , and preferably  $C_1$ - $C_8$ ,

alkyleneoxy radical; Q is a halide ion, preferably chloride; r denotes an average statistical value from 2 to 20, preferably from 2 to 8; s denotes an average statistical value from 20 to 200, and preferably from 20 to 50. These compounds are described in greater detail in US-A-4,185,017. A polymer of this class which is especially preferred is that sold by UNION CARBIDE under the name "UCAR SILICONE ALE 56"(TN).

Another silicone fluid that can be especially useful in the silicone conditioning agents is insoluble silicone gum. The term "silicone gum", as used herein, means polyorganosiloxane materials having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. Silicone gums are described by Petrarch and others including US-A-4,152,416, Spitzer et al., issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane, (polydimethylsiloxane) (methylvinylsiloxane) copolymer, poly(dimethylsiloxane) (diphenyl siloxane)(methylvinylsiloxane) copolymer and mixtures thereof.

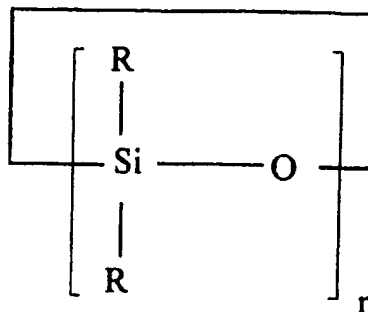
Preferably the silicone hair and /or skin conditioning agent comprises a mixture of a polydimethylsiloxane gum, having a viscosity greater than about 1,000,000 centistokes and polydimethylsiloxane oil having a viscosity of from about 10 centistokes to about 100,000 centistokes, wherein the ratio of gum to fluid is from about 30:70 to about 70:30, preferably from about 40:60 to about 60:40.

Another category of nonvolatile, insoluble silicone fluid conditioning agents are high refractive index silicones, having a refractive index of at least about 1.46, preferably at least about 1.48, more preferably at least about 1.52, most preferably at least about 1.55. Although not intended to necessarily be limiting, the refractive index of the polysiloxane fluid will generally be less than about 1.70, typically



less than about 1.60. Polysiloxane "fluid" includes oils as well as gums.

The high refractive index polysiloxane fluid suitable for purposes hereof includes those represented by general Formula (XIII) above, as well as cyclic polysiloxanes such as those represented by the formula:



wherein R is as defined above, n is from about 3 to about 7, preferably from 3 to 5. The high refractive index polysiloxane fluids hereof contain a sufficient amount of aryl-containing R substituents to increase the refractive index to the desired level, which is described above. In addition, R and n must be selected so that the material is nonvolatile, as defined above.

Aryl-containing substituents contain alicyclic and heterocyclic five and six membered aryl rings, and substituents containing fused five or six membered rings. The aryl rings themselves can be substituted or unsubstituted. Substituents include aliphatic substituents, and can also include alkoxy substituents, acyl substituents, ketones, halogens (e.g., Cl and Br), amines, etc. Exemplary aryl-containing groups include substituted and unsubstituted arenes, such as phenyl, and phenyl derivatives such as phenyls with  $C_1$ - $C_5$  alkyl or alkenyl substituents, e.g., allylphenyl, methyl phenyl and ethyl phenyl, vinyl phenyls such as styrenyl, and phenyl alkynes (e.g. phenyl  $C_2$ - $C_4$  alkynes). Heterocyclic aryl groups include substituents derived from furan, imidazole, pyrrole, pyridine, etc. Fused aryl ring substituents include, for example, naphthalene, coumarin, and purine.

In general, the high refractive index polysiloxane fluids hereof will have a degree of aryl-containing substituents of at least about 15%,

preferably at least about 20%, more preferably at least about 25%, even more preferably at least about 35%, most preferably at least about 50%. Typically, although it is not intended to necessarily limit the invention, the degree of aryl substitution will be less than about 90%, more generally less than about 85%, preferably from about 55% to about 80%.

These polysiloxane fluids are also characterised by relatively high surface tensions as a result of their aryl substitution. In general, the polysiloxane fluids hereof will have a surface tension of at least about 24 dynes/cm<sup>2</sup>, typically at least about 27 dynes/cm<sup>2</sup>. Surface tension, for purposes hereof, is measured by a de Nouy ring tensiometer according to Dow Corning Corporate Test Method CTM 0461, November 23, 1971. Changes in surface tension can be measured according to the above test method or according to ASTM Method D 1331.

The preferred high refractive index polysiloxane fluids hereof will have a combination of phenyl or phenyl derivative substituents (preferably phenyl), with alkyl substituents, preferably C<sub>1</sub>-C<sub>4</sub> alkyl (most preferably methyl), hydroxy, C<sub>1</sub>-C<sub>4</sub> alkylamino (especially -R<sup>1</sup>NHR<sup>2</sup>NH<sub>2</sub> where each R<sup>1</sup> and R<sup>2</sup> independently is a C<sub>1</sub>-C<sub>3</sub> alkyl, alkenyl, and/or alkoxy. High refractive index polysiloxane are available commercially from Dow Corning Corporation (Midland, Michigan, U.S.A.) Huls America (Piscataway, New Jersey, U.S.A.), and General Electric Silicones (Waterford, New York, U.S.A.).

It is preferred to utilise high refractive index silicones in solution with a spreading agent, such as a silicone resin or a surfactant, to reduce the surface tension by a sufficient amount to enhance spreading and thereby enhance glossiness (subsequent to drying) of hair treated with the composition. In general, a sufficient amount of the spreading agent to reduce the surface tension of the high refractive index polysiloxane fluid by at least about 5%, preferably at least about 10%, more preferably at least about 15%, even more preferably at least about 20%, most preferably at least about 25%. Reductions in surface

tension of the polysiloxane fluid/spreading agent mixture can provide improved shine enhancement of the hair.

Also, the spreading agent will preferably reduce the surface tension by at least about 2 dynes/cm<sup>2</sup>, preferably at least about 3 dynes/cm<sup>2</sup>, even more preferably at least about 4 dynes/cm<sup>2</sup>, most preferably at least about 5 dynes/cm<sup>2</sup>.

The surface tension of the mixture of the polysiloxane fluid and the spreading agent, at the proportions present in the final product, is preferably 30 dynes/cm<sup>2</sup> or less, more preferably about 28 dynes/cm<sup>2</sup> or less most preferably about 25 dynes/cm<sup>2</sup> or less. Typically the surface tension will be in the range of from about 15 to about 30, more typically from about 18 to about 28, and most generally from about 20 to about 25 dynes/cm<sup>2</sup>.

The weight ratio of the highly arylated polysiloxane fluid to the spreading agent will, in general, be between about 1000:1 and about 1:1, preferably between about 100:1 and about 2:1, more preferably between about 50:1 and about 2:1, most preferably from about 25:1 to about 2:1. When fluorinated surfactants are used, particularly high polysiloxane: spreading agent ratios may be effective due to the efficiency of these surfactants. Thus is contemplated that ratios significantly above 1000:1 may be used.

References disclosing suitable silicone fluids include US-A-2,826,551, Geen; US-A-3,964,500, Drakoff, issued June 22, 1976; US-A-4,364,837, Pader; and GB-A-849,433, Woolston and 'Silicon Compounds' distributed by Petrarch Systems, Inc., 1984 which provides an extensive (though not exclusive) listing of suitable silicone fluids.

An additional optional ingredient that can be included in the silicone hair and /or skin conditioning agent is silicone resin. Silicone resins are highly cross linked polymeric siloxane systems. The cross linking is introduced through the incorporation of trifunctional and tetrafunctional silanes with monofunctional or difunctional, or both, silanes during manufacture of the silicone resin. As is well understood

in the art, the degree of cross linking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units (and hence, a sufficient level of cross linking) such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of cross linking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinyl-chlorosilanes, and tetrachlorosilane, with the methyl-substituted silanes being most commonly utilised. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art. Background material on silicones including sections discussing silicone fluids, gums, and resins, as well as manufacture of silicones, can be found in Encyclopaedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as "MDTQ" nomenclature. Under this system, the silicone is described according to presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the monofunctional unit  $(\text{CH}_3)_3\text{SiO}_{0.5}$ ; D denotes the difunctional unit  $(\text{CH}_3)_2\text{SiO}$ ; T denotes the trifunctional unit  $(\text{CH}_3)\text{SiO}_{1.5}$ ; and Q denotes the quadri- or tetra-functional unit  $\text{SiO}_2$ . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyls,

amines, hydroxyls, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone (or an average thereof) or as specifically indicated ratios in combination with molecular weight complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of cross linking. As discussed before, however, the overall level of cross linking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MDT and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

The weight ratio of the nonvolatile silicone fluid, having refractive index below 1.46, to the silicone resin component, when used, is preferably from about 4:1 to about 400:1, preferably this ratio is from about 9:1 to about 200:1, more preferably from about 19:1 to about 100:1, particularly when the silicone fluid component is a polydimethylsiloxane fluid or a mixture of polydimethylsiloxane fluid and polydimethylsiloxane gum as described above. Insofar as the silicone resin forms a part of the same phase in the compositions hereof as the silicone fluid, i.e. the conditioning active, the sum of the fluid and resin should be included in determining the level of conditioning agent in the composition.

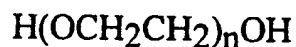
#### Fatty Alcohols

Fatty alcohols suitable for use as conditioning agents for the hair and/or skin herein have the general formula, R-OH, wherein R is a straight or branched chain hydrocarbonyl, preferably straight chain containing from about 8 to about 22 carbon atoms, preferably from about 12 to about 18 carbon atoms. It should be understood that the definition of any particular carbon chain length, say, C<sub>16</sub> is an average value and as such may contain certain proportions of both higher and lower carbon

chain lengths as a direct function of its synthesis. Suitable fatty alcohols for use herein include cetyl alcohol, available under the trade names CO-1695 (TN) from Procter and Gamble Ltd. and Laurex 16 (TN) from Albright and Wilson Ltd.; and stearyl alcohol, available under the trade names CO 1895 (TN) from Procter and Gamble Ltd. and Laurex 18 (TN) from Albright and Wilson Ltd.

#### Water-Soluble Resins

Additional conditioning agents suitable for use herein are water-soluble resins having molecular weights in the range of from about 8,000 to about 2,000,000. Water-soluble, as defined herein means, a material that is sufficiently soluble in water to form a substantially clear solution, to the naked eye, at a concentration of about 0.1% by weight of the material in water at about 25°C. Water-soluble resins useful as conditioning agents herein are nonionic polyethylene glycol polymers having the general formula:



wherein n is an average value of ethoxylation in the range of from about 1000 to about 25,000, preferably from about 2,000 to about 20,000.

Nonionic resins suitable for use herein include narrow molecular weight distribution PEG 14M, available under the trade name Polyox WSRN 3000 (TN) from Amerchol and broad molecular weight PEG 14M available under the trade name Polyox WSR-250 (TN) from Amerchol.

### Polyol Carboxylic Acid Esters

Suitable for use herein as conditioning agents are liquid polyol carboxylic acid esters. These polyol esters are derived from a polyol with one or more carboxylic acids. In other words, these esters contain a moiety derived from a polyol and one or more moieties derived from a carboxylic acid. These carboxylic acid esters can also be described as liquid polyol fatty acid esters, because the terms carboxylic acid and fatty acid are often used interchangeably by those skilled in the art. As used herein, the term liquid, means a fluid which is visibly flowable (to the naked eye) under ambient conditions (about 1 atmosphere of pressure at about 25°C).

The liquid polyol polyesters suitable for use herein comprise certain polyols, especially sugars, sugar alcohols or sugar ethers, esterified with at least two fatty acid groups. The polyol starting material, however, preferably has at least about four esterifiable hydroxyl groups. Examples of preferred polyols are sugars, including monosaccharides and disaccharides, sugar alcohols or sugar ethers. Examples of monosaccharides containing four hydroxyl groups are xylose and arabinose and the sugar alcohol derived from xylose, which has five hydroxyl groups, i.e., xylitol. The monosaccharide, erythrose, is also suitable in the practice of this invention since it contains three hydroxyl groups, as is the sugar alcohol derived from erythrose, i.e., erythritol, which contains four hydroxyl groups. Suitable five hydroxyl group-containing monosaccharides are galactose, fructose, and sorbose. Sugar alcohols containing six hydroxyl groups derived from the hydrolysis products of sucrose, as well as glucose and sorbose, e.g., sorbitol, are also suitable. Examples of disaccharide polyols which can be used include maltose, lactose, and sucrose, all of which contain eight hydroxyl groups. In addition, sugar ethers are also suitable for the practice of this invention, such as, sorbitan.

The polyols used in such liquid polyol esters preferably have from about 4 to about 12, more preferably from about 4 to about 11, and most preferably from about 4 to about 8 hydroxyl groups. Preferred polyols for preparing the polyesters suitable for use herein are selected from the

group consisting of erythritol, xylitol, sorbitol, glucose, and sucrose. Sucrose is especially preferred.

The preferred polyol starting material having at least four hydroxyl groups must be esterified on at least two of the hydroxyl groups with a fatty acid containing from about 8 to about 22 carbon atoms, preferably from about 8 to about 14 carbon atoms. Examples of such fatty acids include caprylic, capric, lauric, myristic, myristoleic, palmitic, palmitoleic, stearic, oleic, ricinoleic, linoleic, linolenic, eleostearic, arachidic, arachidonic, behenic, and erucic acids. The fatty acids can be derived from naturally occurring or synthetic fatty acids; they can be saturated or unsaturated, including positional and geometrical isomers. However, in order to provide liquid polyesters of the type suitable for use herein, at least about half of the fatty acid incorporated into the polyester molecule must be unsaturated fatty acids, saturated short chain fatty acids, or mixtures thereof.

The liquid polyol fatty acid polyesters suitable for use as conditioning agents herein must contain at least two fatty acid ester groups. It is not necessary that all of the hydroxyl groups of the polyol be esterified with fatty acids, but it is preferable that the polyester contain no more than two unesterified hydroxyl groups. Most preferably, substantially all of the hydroxyl groups of the polyol are esterified with fatty acids, i.e., the polyol moiety is substantially completely esterified. The fatty acids esterified to the polyol molecule can be the same or mixed, but as noted above, a substantial amount of the unsaturated acid ester groups and/or saturated short chain acid ester groups must be present to provide liquidity.

To illustrate the above points, a sucrose di-fatty acid ester would be suitable, but is not preferred because it has more than two unesterified hydroxyl groups. A sucrose hexa-fatty acid ester would be preferred because it has no more than two unesterified hydroxyl groups. Highly preferred compounds in which all the hydroxyl groups are esterified with fatty acids include the liquid sucrose octa-substituted fatty acid esters.



The following are non-limiting examples of specific liquid polyol fatty acid polyesters containing at least two fatty acid ester groups suitable for use in the present invention: glucose dioleate, the glucose diesters of soybean oil or cotton seed oil fatty acids (unsaturated), the mannose diesters of mixed soybean oil or cotton seed oil fatty acids, the galactose diesters of oleic acid, the arabinose diesters of linoleic acid, xylose dilinoleate, sorbitol dioleate, sucrose dioleate, glucose trioleate, the glucose triesters of soybean oil or cotton seed oil fatty acids (unsaturated), the mannose triesters of mixed soybean oil or cotton seed oil fatty acids, the galactose triesters of oleic acid, the arabinose triesters of linoleic acid, xylose trilinoleate, sorbitol trioleate, sucrose trioleate, glucose tetraoleate, the glucose tetraesters of soybean oil or cotton seed oil fatty acids (unsaturated), the mannose tetraesters of mixed soybean oil or cotton seed oil fatty acids, the galactose tetraesters of oleic acid, the arabinose tetraesters of linoleic acid, xylose tetralinoleate, galactose pentaoleate, sorbitol tetraoleate, the sorbitol hexaesters of unsaturated soybean oil or cotton seed oil fatty acids, xylitol pentaoleate, sucrose tetraoleate, sucrose pentaoleate, sucrose hexaoleate, sucrose heptaoleate, sucrose octaoleate, and mixtures thereof.

The preferred liquid polyol polyesters of the present invention have complete melting points below about 30°C, preferably below about 27.5°C, and more preferably below about 25°C. Complete melting points reported herein are measured by Differential Scanning Calorimetry (DSC). The term "complete melting point", as used herein means a melting point as measured by the well-known technique of Differential Scanning Calorimetry (DSC). The complete melting point is the temperature at the intersection of the baseline, i.e. the specific heat line, with the line tangent to the trailing edge of the endothermic peak. Typically a scanning temperature of 5°C/minute is used in the present invention in measuring the complete melting points. A technique for measuring complete melting points is more fully described in US-A-5,306,514, to Letton et al., issued April 26, 1994.

Exemplary liquid polyol carboxylic acid esters suitable for use herein are sucrose polysoyate or sucrose polycottonseedoate available from Procter and Gamble.

The polyol fatty acid polyesters suitable for use herein can be prepared by a variety of methods well known to those skilled in the art. These methods include: transesterification of the polyol with methyl, ethyl or glycerol fatty acid esters using a variety of catalysts; acylation of the polyol with a fatty acid chloride; acylation of the polyol with a fatty acid anhydride; and acylation of the polyol with a fatty acid, per se. See US-A-3,463,699, to Rizzi, issued June 15, 1976; and US-A-4,517,360 and 4,518,772 to Volpenhein issued 1985.

### Cationic Polymers

Cationic cellulose derivative polymer materials suitable for use as conditioning agents herein include those having the general formula:



wherein: A is a cellulose anhydroglucose residual, R is an alkylene, oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof, R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> independently are alkyl, aryl, alkylaryl, arylakyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>) preferably being about 20 or less, and M is an anionic counterion, as herein before described.

Suitable cationic cellulosic polymers for use herein have a molecular weight ranging from about 400,000 to about 1,500,000, preferably from about 500,000 to about 1,500,000 and most preferably from about 800,000 to about 1,200,000 and a charge density of from about 0.6 to about 3 meq./gr, preferably from about 0.7 to about 2.0 meq/gr. and most preferably from about 0.9 to about 1.5 meq/gr. Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA)

in their Polymer JR and LR series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10.

The water soluble cationic described herein are either soluble in the shampoo composition, or preferably are soluble in a complex coacervate phase in the shampoo composition formed by the cationic polymer and the anionic surfactant described herein before. Complex coacervates of the cationic polymer can also be formed with other optional anionic components of the shampoo composition.

### Insoluble Oils

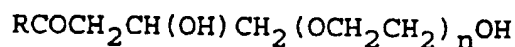
The compositions of the invention may also include an insoluble perfume or cosmetic oil or wax or a mixture thereof as conditioning agents at a level of up to about 10%, preferably up to about 3% by weight. Insoluble oil or wax as defined herein means, the oil or wax is insoluble, in the sense of being insoluble in the product matrix at a temperature of 25°C.

Suitable insoluble cosmetic oils and waxes for use herein as conditioning agents include: C<sub>1</sub>-C<sub>24</sub> esters of C<sub>8</sub>-C<sub>30</sub> fatty acids such as isopropyl myristate, myristyl myristate and cetyl ricinoleate, C<sub>8</sub>-C<sub>30</sub> esters of benzoic acid, beeswax, saturated and unsaturated fatty alcohols such as behenyl alcohol, hydrocarbons such as mineral oils, petrolatum squalane and squalene, polybutene, fatty sorbitan esters (see US-A-3,988,255, Seiden, issued October 26th 1976), lanolin and oil-like lanolin derivatives, animal and vegetable triglycerides such as almond oil, peanut oil, wheat germ oil, rice bran oil, linseed oil, jojoba oil, oil of apricot pits, walnuts, palm nuts, pistachio nuts, sesame seeds, rapeseed, cade oil, corn oil, peach pit oil, poppyseed oil, pine oil, castor oil, soyabean oil, avocado oil, safflower oil, coconut oil, hazelnut oil, olive oil, grapeseed oil, and sunflower seed oil, and C<sub>1</sub>-C<sub>24</sub> esters of dimer and trimer acids such as diisopropyl dimerate, diisostearylmalate, diisostearyldimerate and triisostearyltrimerate and mixtures thereof.

### Oil Derived Materials

The compositions of the invention may also contain an oil derived conditioning agent or mixture of oil derived conditioning agent. Suitable oil derived conditioning agents for use herein include water soluble vegetable and animal-derived emollients such as triglycerides with a polyethyleneglycol chain inserted; ethoxylated mono and diglycerides, polyethoxylated lanolins and ethoxylated butter derivatives. One preferred class of oil derived conditioning agents for use herein having the general formula:

O



wherein n is from about 5 to about 200, preferably from about 20 to about 100, more preferably from about 30 to about 85, and wherein R comprises an aliphatic radical having on average from about 5 to 20 carbon atoms, preferably from about 7 to 18 carbon atoms.

Suitable ethoxylated oils and fats of this class include polyethyleneglycol derivatives of glyceryl cocoate, glyceryl caproate, glyceryl caprylate, glyceryl tallowate, glyceryl palmate, glyceryl stearate, glyceryl laurate, glyceryl oleate, glyceryl ricinoleate, and glyceryl fatty esters derived from triglycerides, such as palm oil, almond oil, and corn oil, preferably glyceryl tallowate and glyceryl cocoate.

Suitable oil derived conditioning agents of this class are available from Croda Inc. (New York, USA) under their Crovol (TN) line of materials such as Crovol EP40 (PEG 20 evening primrose glyceride), Crovol EP 70 (PEG 60 evening primrose glyceride) Crovol A-40 (PEG 20 almond glyceride), Crovol A-70 (PEG 60 almond glyceride), Crovol M-40 (PEG 20 maize glyceride), Crovol M-70 (PEG 60 maize glyceride), Crovol PK-40 (PEG 12 palm kernel glyceride), and Crovol PK-70 (PEG 45 palm kernel glyceride) and under their Solan (TN) range of materials such as Solan E, E50 and X polyethoxylated lanolins and Aqualose L-20 (TN) (PEG 24 lanolin alcohol) and Aqualose W15 (TN) (PEG 15 lanolin alcohol) available from Westbrook Lanolin.

Further suitable surfactants of this class are commercially available from Sherex Chemical Co. (Dublin, Ohio, USA) under their Varonic LI (TN) line of surfactants and from Rewo under their Rewoderm (TN) line of surfactants. These include, for example, Varonic LI 48 (polyethylene glycol (n=80) glyceryl tallowate, alternatively referred to as PEG 80 glyceryl tallowate), Varonic LI 2 (PEG 28 glyceryl tallowate), Varonic LI 420 (PEG 200 glyceryl tallowate), and Varonic LI 63 and 67 (PEG 30 and PEG 80 glyceryl cocoates), Rewoderm LI5-20 (PEG-200 palmitate), Rewoderm LIS-80 (PEG-200 palmitate with PEG-7 glyceryl cocoate) and Rewoderm LIS-75 (PEG-200 palmitate with PEG-7 glyceryl cocoate) and mixtures thereof. Other oil-derived emollients suitable for use are PEG derivatives of corn, avocado, and babassu oil, as well as Softigen 767 (TN) (PEG(6) caprylic/capric glycerides).

Also suitable for use herein are conditioning oils derived from composite vegetable fats extracted from the fruit of the Shea Tree (*Butyrospermum Karkii* Kotschy) and derivatives thereof. This vegetable fat, known as Shea Butter is widely used in Central Africa for a variety of means such as soap making and as a barrier cream, it is marketed by Sederma (78610 Le Perray En Yvelines, France). Particularly suitable are ethoxylated derivatives of Shea butter available from Karlshamn Chemical Co. (Columbus, Ohio, USA) under their Lipex (TN) range of chemicals, such as Lipex 102 E-75 and Lipex 102 E-3 (ethoxylated mono, di-glycerides of Shea butter) and from Croda Inc. (New York, USA) under their Crovol (TN) line of materials such as Crovol SB-70 (ethoxylated mono, di-glycerides of Shea butter). Similarly, ethoxylated derivatives of Mango, Cocoa and Illipe butter may be used as conditioning agents in the compositions according to the invention. Although these are classified as ethoxylated nonionic materials it is understood that a certain proportion may remain as non-ethoxylated vegetable oil or fat.

Other suitable oil derived hair and / or skin conditioning agents include ethoxylated derivatives of almond oil, peanut oil, rice bran oil, wheat germ oil, linseed oil, jojoba oil, oil of apricot pits, walnuts, palm nuts, pistachio nuts, sesame seeds, rapeseed, cade oil, corn oil, peach pit

oil, poppyseed oil, pine oil, castor oil, soybean oil, avocado oil, safflower oil, coconut oil, hazelnut oil, olive oil, grapeseed oil, and sunflower seed oil.

Oil derived hair and /or skin conditioning agents highly preferred for use herein include Lipex 102-3 (TN) (PEG-3 ethoxylated derivatives of Shea Butter) and Softigen 767 (TN) (PEG-6 caprylic/capric glycerides).

### Styling Agents

The shampoo compositions according to the present invention may also contain as an additional optional cosmetic agent one or more styling agents. Styling agents suitable for use herein are a class of materials which are designed to assist the user in having the shampooed hair retain a particular shape.

Hair styling agents suitable for use herein can be selected from various resins and gums. Preferred styling agents used herein comprise shampoo compatible polymers which, in general, are homopolymers or copolymers of hydrophobic monomers. Alternatively, hydrophilic polymers useful as styling agents herein can be a copolymer of a hydrophilic monomer and a hydrophobic monomer, or mixtures thereof. Examples of complex polymer systems are found in US-A-3,222,329, US-A-3,577,517, US-A-4,272,511 and US-A-4,196,190. Examples of block polymer systems are found in US-A-3,907,984, US-A-4,030,512 and US-A-4,283,384.

### Pharmaceutical active

Pharmaceutical actives may be utilised in the compositions herein for the provision of additional benefits to the hair and /or skin include anti-lice actives, anti-biotics, anti-inflammatory actives and anti-dandruff actives. Pharmaceutical active, as defined herein, includes both pharmaceutical and drug actives.

### Particulate Anti-Dandruff Active

The shampoo compositions may contain one or more particulate anti dandruff agents as a pharmaceutical active. A safe and effective amount of anti dandruff active for control of dandruff on the scalp is used. Particulate anti dandruff agents include, for example, sulfur, selenium sulfide, and pyridinethione salts. Preferred are heavy metal salts of 1-hydroxy-2-pyridinethione and selenium disulfide. The particulate anti dandruff agents are in crystalline form and are insoluble in the compositions. In general, particulate anti dandruff agents are used at levels of about 0.1% to about 5%, preferably from about 0.3% to about 5%, by weight of the composition. The particular amount used is not critical as long as an effective amount is used for controlling dandruff when the composition is used to shampoo the skin or hair in the conventional manner.

Selenium sulfide is a staple item of commerce. Selenium sulfide is generally regarded as a compound having one mole of selenium and two moles of sulfur. However, it may take the form of a cyclic structure,  $Se_xS_y$ , wherein  $x + y = 8$ . US-A-2,694,668, Baldwin et al., issued November 16, 1954; US-A-3,152,046, Kapral, issued October 6, 1984; US-A-4,089,945, Brinkman, issued May 16, 1978; and US-A-4,885,107, Wetzell, issued December 12, 1989 disclose selenium disulfide as an active ingredient in anti dandruff shampoo compositions.

Selenium sulfide (selenium disulfide) preferably has an average of less than about  $15\mu$ , more preferably less than about  $10\mu$ . These measurements can be made using a forward laser light scattering device (e.g., a Malvern 3600 instrument). If used, selenium sulfide is typically present in the shampoo compositions of this invention at a level of from about 0.1% to about 5.0%, preferably from about 0.3% to about 2.5%, more preferably from about 0.5% to about 1.5%, by weight of the composition.

Preferred pyridinethione anti dandruff agents are water insoluble 1-hydroxy-2-pyridinethione salts. Preferred salts are formed from heavy metals such as zinc, tin, cadmium, magnesium, aluminium and zirconium. The most preferred metal herein is zinc. The most preferred

active is the zinc salt of 1-hydroxy-2-pyridinethione, often referred to as zinc pyridinethione (ZPT). Other cations such as sodium may also be suitable. These types of anti dandruff agents are well known in the art. 1-hydroxy-2-pyridinethione salts are disclosed for use in anti dandruff shampoos in US-A-2,809,971, Bernstein, issued October 15, 1957; US-A-3,236,733, Karsten et al., issued February 22, 1966; US-A-3,753,196 Parran, issued August 21, 1973; US-A-3,761,418, Parran, issued September 25, 1973; US-A-4,345,080, Bolich, issued August 17, 1982; US-A-4,323,683, Bolich et al., issued April 6, 1982; US-A-4,379,753, Bolich, issued April 12, 1983; and US-A-4,470,982, Winkler, issued September 11, 1984. Particularly preferred are those 1-hydroxy-2-pyridinethione salts in platelet particle form, wherein the particles have an average size of up to about 20 microns, preferably up to about 8 microns, most preferably up to about 5 microns.

The pyridinethione salts are generally used at a level of from about 0.1% to about 3%, preferably about 0.3% to about 2%, by weight of the shampoo composition.

Other particulate anti dandruff actives include sulfur. Sulfur is typically used as an anti dandruff agent at a level of from about 1% to about 5%, more preferably from about 2% to about 5%, by weight of the composition.

#### Suspending Agent

The present compositions can include a crystalline suspending agent. Other suspending agents useful for suspending the conditioning agents (or other materials) and for thickening the compositions can optionally be used. The crystalline suspending agent serves to assist in suspending the dispersed phase fluid conditioning agent, or other particulate matter or emulsions of insoluble fluids, in the shampoo compositions hereof, and may give pearlescence to the product.

The crystalline suspending agent will be used at an effective level for suspending the conditioning agent or particulate anti dandruff agent (if present). The suspension should, in general, be stable for at least one



month at ambient temperature. Longer term shelf stability such as at least three months, preferably six months, most preferably at least about twenty-four months, is preferred. In general, the compositions hereof will comprise from about 0.5% to about 10%, by weight, of a crystalline suspending agent or combination thereof. The crystalline suspending agent is preferably present in the shampoo compositions hereof at a level of about 0.5% to about 5%, more preferably about 1% to about 4%, most preferably about 1% to about 3% by weight.

Preferred crystalline suspending agents are acyl derivatives and amine oxides, especially acyl derivatives, especially those which can be solubilized in a premix solution and then be recrystallized upon cooling. These materials will comprise long chain (e.g., C<sub>8</sub>-C<sub>22</sub> preferably C<sub>14</sub>-C<sub>22</sub>, more preferably C<sub>16</sub>-C<sub>22</sub>) aliphatic groups, i.e., long chain acyl derivative materials and long chain amine oxides, as well as mixtures of such materials. Included are ethylene glycol long chain esters, alkanol amides of long chain fatty acids, long chain esters of long chain fatty acids, glyceryl long chain esters, long chain esters of long chain alkanolamides, and long chain alkyl dimethyl amine oxides, and mixtures thereof.

Examples of crystalline suspending agents are described in US-A-4,741,855, Grote and Russell, issued May 3, 1988. Suitable suspending agents for use herein include ethylene glycol esters of fatty acids preferably having from about 14 to about 22 carbon atoms, more preferably 16-22 carbon atoms. More preferred are the ethylene glycol stearates, both mono and distearate, but particularly the distearate containing less than about 7% of the mono stearate. Other suspending agents include alkanol amides of fatty acids, preferably having from about 16 to about 22 carbon atoms, more preferably about 16 to 18 carbon atoms. Preferred alkanol amides are stearic monoethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic monoethanolamide stearate polyethylene glycol esters of a fatty acid having from about 16 to about 22 carbon atoms and up to 7 ethyleneoxy units, preferably the ethylene glycol stearates, both mono and distearate, but particularly the distearate containing less than about 7% of the mono stearate, alkanolamides of fatty acids, having from about 16 to

about 22 carbon atoms, preferably about 16 to 18 carbon atoms such as stearic monoethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic monoethanolamide. Other long chain acyl derivatives include long chain esters of long chain fatty acids (e.g., stearyl stearate, cetyl palmitate); glyceryl esters (e.g., glyceryl distearate) and long chain esters of long chain alkanol amides (e.g., stearamide diethanolamide distearate, stearamide monoethanolamide stearate). Ethylene glycol esters of long chain carboxylic acids, long chain amine oxides, and alkanol amides of long chain carboxylic acids, in addition to the preferred materials listed above, may be used as suspending agents.

Suspending agents also include long chain amine oxides such as alkyl (C<sub>16</sub>-C<sub>22</sub>) dimethyl amine oxides, e.g., stearyl dimethyl amine oxide. If the compositions contain an amine oxide or a long chain acyl derivative which is a surfactant, the suspending function could also be provided by such amine oxide or acyl derivative, provided at least a portion of them are present in crystalline form, and additional suspending agent may not be needed.

Other long chain acyl derivatives that can be used include N,N-dihydrocarbyl (C<sub>12</sub>-C<sub>22</sub>, preferably C<sub>16</sub>-C<sub>18</sub>) amido benzoic acid and soluble salts thereof (e.g., Na and K salts), particularly N,N-di(C<sub>16</sub>-C<sub>18</sub>, and hydrogenated tallow) amido benzoic acid species of this family, which are commercially available from Stepan Company (Northfield, Illinois, USA).

Further suitable suspending agents include fatty alcohol or fatty acid materials having from about 12 to about 22 carbon atoms. Suitable fatty acid and fatty alcohol thickeners include Laurex NC (TN) (C<sub>12</sub>/14 fatty alcohol) available from Albright and Wilson and Prifac 7908 (TN) (palm kernel fatty acid) available from Unichema. Also suitable for use herein as suspending agents are fatty acid esters of glucosides such as PEG 120 methyl glucoside dioleate (available from Amercol under the trade name Glucamate DOE 120 (TN)).

The crystalline suspending agent can be incorporated into the shampoos hereof by solubilizing it into a solution containing water and surfactant at a temperature above the melting point of the suspending agent. The suspending agent is then recrystallized, typically by cooling the solution to a temperature sufficient to induce crystallization.

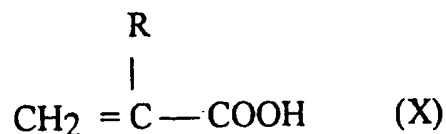
Optional suspending agent thickeners, and viscosity modifiers, etc., when used are in general used at a level of from about 0.01% to about 10%, most commonly from about 0.02% to about 5.0% by weight of the total composition. In general, the level of optional suspending agent and other viscosity modifiers should preferably be as low as possible to achieve the benefit for which the material is added.

Optional suspending agents that can be used include polymeric thickeners, such as carboxyvinyl polymers. Preferred carboxyvinyl polymers include acrylic acid/ethyl acrylate copolymers and the carboxyvinyl polymers sold by the B.F. Goodrich Company under the trade mark of Carbopol resins, such as, the copolymers of acrylic acid cross linked with polyallylsucrose as described in US-A-Patent 2,798,053, Brown, issued July 2, 1957. These polymers are provided by B. F. Goodrich Company as, for example, Carbopol (TN) 934, 940, 941, and 956. These resins consist essentially of a colloiddally water-soluble polyalkenyl polyether cross linked polymer of acrylic acid cross linked with from 0.75% to 2.00% of a cross linking agent such as for example polyallyl sucrose or polyallyl pentaerythritol. Examples include Carbopol 934, Carbopol 940, Carbopol 950, Carbopol 980, Carbopol 951 and Carbopol 981. Carbopol 934 is a water-soluble polymer of acrylic acid cross linked with about 1% of a polyalkyl ether of sucrose having an average of about 5.8 allyl groups for each sucrose molecule. Also suitable for use herein are hydrophobically-modified cross-linked polymers of acrylic acid having amphipathic properties available under the Trade Name Carbopol 1382, Carbopol 1342 and Pemulen TR-1 (CFTA Designation: Acrylates/10-30 Alkyl Acrylate Crosspolymer). A combination of the polyalkenyl polyether cross-linked acrylic acid polymer and hydrophobically modified cross-linked acrylic acid polymer is also suitable for use herein.

A carboxyvinyl polymer is an interpolymer of a monomeric mixture comprising a monomeric olefinically unsaturated carboxylic acid, and from about 0.01% to about 10% by weight of the total monomers of a polyether of a polyhydric alcohol, which polyhydric alcohol contains at least four carbon atoms to which are attached at least three hydroxyl groups, the polyether containing more than one alkenyl group per molecule. Other monoolefinic monomeric materials may be present in the monomeric mixture if desired, even in predominant proportion. Carboxyvinyl polymers are substantially insoluble in liquid, volatile organic hydrocarbons and are dimensionally stable on exposure to air.

Preferred polyhydric alcohols used to produce carboxyvinyl polymers include polyols selected from the class consisting of oligosaccharides, reduced derivatives thereof in which the carbonyl group is converted to an alcohol group, and pentaerythritol; more preferred are oligosaccharides, most preferred is sucrose. It is preferred that the hydroxyl groups of the polyol which are modified be etherified with allyl groups, the polyol having at least two allyl ether groups per polyol molecule. When the polyol is sucrose, it is preferred that the sucrose have at least about five allyl ether groups per sucrose molecule. It is preferred that the polyether of the polyol comprise from about 0.01% to about 4% of the total monomers, more preferably from about 0.02% to about 2.5%.

Preferred monomeric olefinically unsaturated carboxylic acids for use in producing carboxyvinyl polymers used herein include monomeric, polymerizable, alpha-beta monoolefinically unsaturated lower aliphatic carboxylic acids; more preferred are monomeric monoolefinic acrylic acids of the structure (X):



where R is a substituent selected from the group consisting of hydrogen and lower alkyl groups; most preferred is acrylic acid.

Preferred carboxyvinyl polymers used in formulations of the present invention have a molecular weight of at least about 750,000; more preferred are carboxyvinyl polymers having a molecular weight of at least about 1,250,000; most preferred are carboxyvinyl polymers having a molecular weight of at least about 3,000,000.

Other materials can also be used as optional suspension agents include those that can impart a gel-like viscosity to the composition, such as water soluble or colloiddally water soluble polymers like cellulose ethers (e.g., hydroxyethyl cellulose), guar gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives, and other thickeners, viscosity modifiers, gelling agents, etc. Mixtures of these materials can also be used.

Another type of suspending agent that can be used is xanthan gum. Shampoo compositions utilising xanthan gum as a suspending agent for the silicone hair conditioning component are described in US-A-4,788,006, Bolich and Williams, issued November 29, 1988. Xanthan gum is biosynthetic gum material that is commercially available. It is a heteropolysaccharide with a molecular weight of greater than 1 million. It is believed to contain D-glucose, D-mannose and D-glucuronate in the molar ratio of 2.8:2.0:2.0. The polysaccharide is partially acetylated with 4.7% acetyl. This information and other is found in Whistler, Roy L. Editor *Industrial Gums - Polysaccharides and Their Derivatives* New York: Academic Press, 1973. Kelco, a Division of Merck & Co., Inc. offers xanthan gum as Keltrol R (TN). The gum, when used as the silicone hair conditioning component suspending agent, will typically be present in pourable, liquid formulations at a level of from about 0.02% to about 3%, preferably from about 0.03% to about 1.2% by weight of the compositions of the present invention.

Optional Ingredients

A variety of other optional ingredients are described herein. The following description is exemplary in nature.

### Thickening Agent

The shampoo compositions of the present invention may additionally include one or more thickening agents at a total level of from about 0.1% to about 10%, preferably from about 0.5% to about 5%, more preferably from about 0.5% to about 3% by weight.

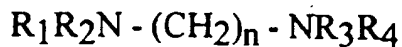
Nonionic water-soluble cellulose ethers can be used as thickening agents in the compositions according to the present inventions. Widely used, commercially-available nonionic cellulose ethers include methyl cellulose, hydroxy propyl methyl cellulose, hydroxyethylcellulose, hydroxypropyl cellulose and ethyl hydroxyethyl cellulose. Particularly preferred for use as thickening agents are hydrophobically modified hydroxy ethyl cellulose materials. One commercially available material suitable for use herein is NATROSOL PLUS Grade 330 CS (TN), a hydrophobically modified hydroxyethylcellulose available from Aqualon Company, Wilmington, Delaware. This material has a C<sub>16</sub> alkyl substitution of from 0.4% to 0.8% by weight. The hydroxyethyl molar substitution for this material is from 3.0 to 3.7. The average molecular weight for the water-soluble cellulose prior to modification is approximately 300,000. Another material of this type is sold under the trade name NATROSOL PLUS CS Grade D-67 (TN), by Aqualon Company, Wilmington, Delaware. This material has a C<sub>16</sub> substitution of from 0.50% to 0.95%, by weight. The hydroxyethyl molar substitution for this material is from 2.3 to 3.7. The average molecular weight for the water soluble cellulose prior to modification is approximately 700,000.

The compositions according to the present invention can also comprise a urethane based polyethylene glycol copolymer thickening agent such as urethane C<sub>1</sub>-C<sub>20</sub> alkyl PEG copolymer available from Rohm and Haas under the trade name Acrosyl 44 (TN). Such urethane based copolymer thickeners are valuable for both the delivery of excellent thickening properties and improved lathering characteristics with maintenance of desirable rinse feel attributes.

The present compositions can also comprise a nonionic or anionic polymeric thickening component, especially a water-soluble polymeric materials, having a molecular weight greater than about 20,000. By "water-soluble polymer" is meant that the material will form a substantially clear solution in water at a 1% concentration at 25°C and the material will increase the viscosity of the water. Examples of water-soluble polymers which may desirably be used as an additional thickening component in the present compositions, are hydroxyethylcellulose, hydroxypropyl cellulose, hydroxypropyl methylcellulose, polyethylene glycol, polyacrylamide, polyacrylic acid, polyvinyl alcohol, polyvinyl pyrrolidone K-120, dextrans, for example Dextran purified crude Grade 2P, available from D&O Chemicals, carboxymethyl cellulose, plant exudates such as acacia, ghatti, and tragacanth, seaweed extracts such as sodium alginate, propylene glycol alginate and sodium carrageenan. Preferred as the additional thickeners for the present compositions are natural polysaccharide materials. Examples of such materials are guar gum, locust bean gum, and xanthan gum. Also suitable herein preferred is hydroxyethyl cellulose having a molecular weight of about 700,000.

#### Diamine Dipolyacid Component

As additional optional feature the compositions of the present invention may comprise a diamine dipolyacid component and /or salts thereof. Dipolyacid, as defined herein means diacids, triacids and tetraacids and salts thereof and is preferably a diacid. Diamine dipolyacids suitable for use herein can be synthesised, for example, by the reaction of a diamine with an anhydride. Diamine starting materials for the preparation of diamine dipolyacids include diamines having the general formula:



wherein  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are selected from hydrogen and  $C_1$  to  $C_4$  alkyl or alkenyl, preferably wherein  $R_1$  and  $R_3$  are hydrogen, more preferably where  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are hydrogen;  $n$  is an integer from 1 to 8, preferably from 2 to 4 and especially 2. Preferred diamines for



use herein include ethylene diamine, 1,3-propylene diamine, 1,4-butanediamine, especially preferred is ethylene diamine. Any anhydride which is capable of reacting with a diamine, as defined above, to form a diamine dipolyacid may be used herein. An exemplary anhydride suitable for use herein is maleic anhydride.

Diamine dipolyacid materials suitable for use herein can also be synthesised, for example, by reaction of a diacid with a dihalogen substituted hydrocarbyl under alkaline conditions (for example, sodium hydroxide solution at pH about 11.2), as discussed in WO-A-95/12570, WO-A-96/01803, WO-A-96/01802, and US-A-5,466,867. Diacid starting materials suitable for use herein include amino acids (or salts thereof) such as L-aspartic acid. Dihalogen substituted hydrocarbyls suitable for use herein have the general formula:



wherein X and Y are halogens, such as, Br, Cl, preferably X and Y are both Br or Cl, n has a value of from 2 to about 8, preferably from 2 to 6, more preferably from 2 to 4. Exemplary dihalogen substituted hydrocarbyls suitable for use herein include ethylene dibromide and ethylene dichloride.

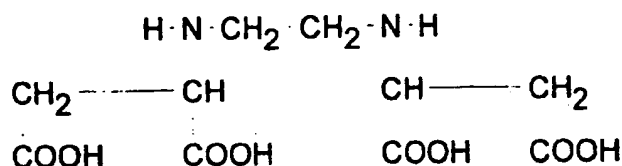
Preferred for use herein are diamine dipolyacids wherein the polyacid species is a diacid, preferably a diacid having a hydrocarbyl chain length of from about 3 to about 10 carbon atoms, more preferably from about 4 to about 6 carbon atoms, and most preferably about 4 carbon atoms. Exemplary diamine dipolyacids, derived from diacids, suitable for use herein include ethylene diamino disuccinic acid (EDDS), ethylenediamine diglutamic acid (EDDG) and 2-hydroxypropylenediamine disuccinic acid (HPDDS) as disclosed in US-Patent Application No 08/026,884.

Highly preferred for use herein is ethylene diamine disuccinic acid (EDDS). Preferred EDDS compounds for use herein are the free acid form and the sodium or magnesium salt thereof. Examples of

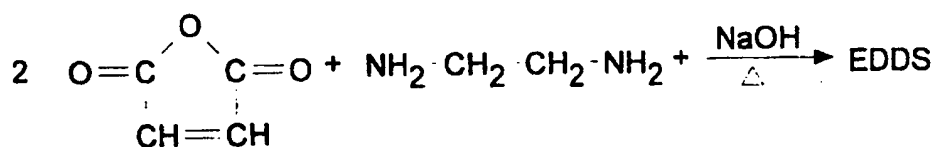
such preferred sodium salts of EDDS include  $\text{Na}_2$  EDDS and  $\text{Na}_3$  EDDS.

The sodium complexes are the most preferred for inclusion in shampoo compositions in accord with the invention. These complexes may be added to the compositions as such, or they may be formed during the process for making the composition by the reaction of an inert sodium salt such as  $\text{NaCl}$  or  $\text{Na}_2\text{SO}_4$  with an EDDS compound added as either the acid, or as a salt or complex. Where the EDDS compound is added in the making process, together with the inert sodium salt, it is preferred that the molar ratio of sodium to EDDS should be greater than 1:1, preferably greater than 3:1, to ensure formation of the desired sodium complexes.

The structure of the acid form of EDDS is as follows:



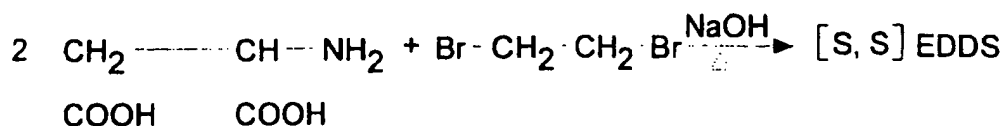
EDDS can be synthesised, for example, from readily available, inexpensive starting materials such as maleic anhydride and ethylenediamine as follows.



A more complete disclosure of methods for synthesising EDDS from commercially available starting materials can be found in US-A-3,158,635, Kezerian and Ramsay, issued November 24, 1964.

The synthesis of EDDS from maleic anhydride and ethylene diamine yields a mixture of three optical isomers, [R,R], [S,S], and [S,R], due to the two asymmetric carbon atoms. The biodegradation of EDDS is optical isomer-specific, with the [S,S] isomer degrading most rapidly and extensively.

The [S,S] isomer of EDDS can be synthesised from L-aspartic acid and 1,2-dibromoethane, as follows.



A more complete disclosure of the reaction of L-aspartic acid with 1,2-dibromoethane to form the [S,S] isomer of EDDS can be found in Neal and Rose, Stereospecific Ligands and Their Complexes of Ethylenediamine-discuccinic Acid, Inorganic Chemistry, Vol. 7 (1968), pp. 2405-2412.

EDDS can also be prepared by fermentation using a strain of *Actinomycetes* (MG417-CF17), preferably inhibited with phospholipase C & D, as detailed in Inst. Microb. Chem., Tokyo, 141, Japan.

A preferred form of EDDS suitable for inclusion herein is an aqueous solution of the [S,S] isomer of EDDS, neutralised with sodium hydroxide, wherein about 30% of the EDDS remaining as the free acid, and wherein the EDDS complex is present as the tri-sodium salt and forms at least about 95% of the total amine carboxylates species. This species is available from the Palmer Research Laboratories a division of Associated Octel. Diamine dipolyacid can be included in the compositions of the present invention at a total level of from about 0.001% to about 10% by weight.

The viscosity of the final composition (Brookfield DV II + (or DV II), 1 rpm with Cone CP41 or CP52, 3 mins at 26.7°C, neat) is preferably at least about 500 cps, more preferably from about 1,000 to about 50,000 cps, especially from about 1,000 to about 30,000 cps, more especially from about 1,000 to about 8,000 cps.

Additional optional ingredients include, for example, preservatives such as sodium benzoate, DMDM hydantoin, benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea;

cationic conditioning agents, including both cationic conditioning surfactants and cationic conditioning polymers; quaternary polymeric foam boosters, such as Polyquaternium 10, preferably at a level of from about 0.01% to about 0.2%, by weight of the composition; fatty alcohols; block polymers of ethylene oxide and propylene oxide such as Pluronic F88 (TN) offered by BASF Wyandotte; sodium chloride, sodium sulfate; ammonium xylene sulfonate; propylene glycol; polyvinyl alcohol; ethyl alcohol; pH adjusting agents such as monosodiumphosphates, disodium phosphates, citric acid, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate, etc.; sequestering agents such as EDTA etc.; electrolyte such as magnesium sulfate; perfumes; and dyes. These optional ingredients are typically used at levels of from about 0.01% to about 10% of the composition. This list of optional ingredients is not meant to be exclusive, and other optional components can be utilised.

#### Water

The compositions of the present invention will comprise from about 20% to about 98.8%, preferably from about 50% to about 85%, more preferably from about 60% to about 85%, by weight, of water.

The pH of the compositions hereof is preferably in the range of from 2 to about 10, preferably from about 4 to about 9, more preferably from about 5 to about 7.

The invention hereof will generally not include detergent compositions for laundry applications containing conventional laundry detergent additives, such as, enzymes, brighteners, dye transfer inhibition agents and the like.

The invention is illustrated by the following non-limiting examples. In the examples, all concentrations are on a 100% active basis and the abbreviations have the following designation:

- |                     |  |
|---------------------|--|
| Short Chain AS      | Sodium C10 alkyl sulfate (available from Albright and Wilson (A & W) as Empicol LC35 (TN))       |
| Ethoxy Alcohol      | Ethoxylated fatty alcohol (available from Shell as Dobanol 91-8 (TN))                            |
| Auxiliary Anionic 1 | Ammonium laureth-3 sulfate (available from A & W as Empicol EAC/TP (TN))                         |
| Auxiliary Anionic 2 | Narrow Range sodium laureth 3 sulfate (available from Hoechst as Genapol ZRO narrow range (TN)). |
| Amphoteric 1        | Cocoamidopropyl hydroxy sultaine (available from Rhone-Poulenc as Miritaine CBS (TN))            |
| Amphoteric 2        | Cocoamidopropyl dimethyl carboxymethyl betaine (from TH Goldschmidt as Tegobetane F (TN))        |
| Conditioner 1       | Dimethicone 40:60 (CF1233 from GE Silicones)   |
| Conditioner 2       | Cetyl alcohol (Laurex 16 (TN) from A & W)  |
| Conditioner 3       | Stearyl Alcohol (Laurex 18 (TN) from A & W)  |
| Conditioner 4       | Hydroxyethylcellulose with epichlorohydrin and trimethylamine (Polymer LR-400(TN) /Amerchol)     |
| Conditioner 5       | Nonionic PEG 14 M resin (available from Amerchol as Polyox WSRN 3000 (TN))                       |

In addition to the above, the compositions may additionally include, thickening agents such as sodium chloride and suspending agents, such

as, ethylene glycol distearate EGDS (available as Radi 7266 (TN) from Faci) as well as perfumes, dyes and other minors

### Examples I to XII

The following are cleansing compositions in the form of shampoo products and which are non-limiting representations of the present invention:

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Short Chain	5	5	5	2	4	3	6	2	10	3	4	4
AS												
Ethoxy	2	3	2	5	4	4	6	5	5	5	3	8
Alcohol												
Auxiliary	-	10	-	10	-	-	-	15	-	-	-	-
Anionic 1												
Auxiliary	5	-	5	-	5	6	-	-	-	12	12	3
Anionic 2												
Amph. 1	-	2	5	-	3	-	-	-	5	3	-	-
Amph. 2	5	-	-	5	-	4	6	5	5	-	3	6
Cond. 1	0.5	-	0.7	0.8	-	0.3	0.5	1.5	0.4	0.3	0.5	0.7
Cond. 2	0.1	0.5	0.1	0.1	0.3	-	-	-	0.4	-	-	0.1
				5								
Cond. 3	0.5	-	0.5	-	0.4	0.3	0.18	0.3	0.2	0.4	-	-
Cond. 4	-	0.5	-	-	0.1	0.5	-	-	-	-	0.2	-
Cond. 5	-	0.2	-	0.1	-	-	-	0.3	-	-	-	-
		5										
Thickener	0.5	-	0.2	-	-	-	0.5	-	-	-	0.4	0.1
			5									
EGDS	1.5	1.0	0.1	2.0	2.5	0.5	1.0	1.0	-	1.5	1.0	2.0
Water						to	100					

The shampoo compositions herein can be made by preparing in a premix tank the short chain alkyl sulphate surfactant and ethoxylated alcohol nonionic surfactant and other, auxiliary surfactants with part of the water while mixing and heating to about 72°C. Once the temperature reaches about 72°C the fatty alcohols, tetra sodium EDTA, citric acid, ethylene glycol distearate and sodium benzoate can be added with further mixing. Conditioning polymers, where present, may be added at this point. After at least about 30 minutes mixing the mixture is cooled to about 32°C (for example, by passing through a heat exchanger). The following materials can then be added to the cooled mixture, diaminedipolyacid, remaining polymers, dimethicone blend (where present), sodium chloride, perfume, other conditioning agents and water & minors.

Thus according to a yet further aspect of the present invention there is provided a method of making a shampoo composition wherein short chain alkyl sulphate is combined with ethoxylated alcohol and auxiliary surfactant and water.

The shampoo compositions of the invention are valuable for the provision of improved rinsibility, excellent cleansing, and improved hair conditioning characteristics such as hair feel, hair shine, hair volume and manageability.

What is claimed is:

1. A shampoo composition comprising:
  - (a) from about 0.1% to about 10% by weight of short chain alkyl sulfate surfactant having a carbon chain length of 10 carbon atoms or less.
  - (b) from about 0.1% to about 10% by weight of ethoxylated alcohol; and
  - (c) from about 1% to about 60% by weight of auxiliary surfactant selected from anionic surfactant other than the short chain alkyl sulfate of (a), nonionic surfactant other than the ethoxylated alcohol of (b), amphoteric and cationic surfactants and mixtures thereof;
  - (d) water.
2. A composition according to Claim 1 wherein at least about 50% by weight of the short chain alkyl sulphate surfactant comprises C<sub>10</sub> short chain alkyl sulfate or less.
3. A composition according to both of Claims 1 and 2 wherein at least about 50% by weight of the short chain alkyl sulphate comprises C<sub>8</sub> to C<sub>10</sub> short chain alkyl sulphate.
4. A composition according to any of Claims 1 to 3 wherein at least about 50% by weight of the short chain alkyl sulphate comprises C<sub>10</sub> short chain alkyl sulphate.
5. A composition according to any of Claims 1 to 4 wherein the short chain alkyl sulfate material contains at least about 80%, preferably at least about 90%, more preferably at least about 95 %, most preferably at least about 97% by weight of C<sub>10</sub> alkyl sulfate.



6. A composition according to any of Claims 1 to 5 wherein the level of short chain alkyl sulfate is from about 0.5% to about 8%, more preferably from about 1% to about 6%, most preferably from about 2% to about 4% by weight.
7. A composition according to any of Claims 1 to 6 wherein the level of short chain alkyl sulfate surfactant is at least about 0.5%, more preferably at least about 1% and most preferably at least about 2% by weight.
8. A composition according to any of Claims 1 to 7 wherein the ethoxylated alcohol surfactant is selected from monohydric, dihydric and polyhydric alcohol mono- and poly- ethoxylates and / or alkylated derivatives thereof.
9. A composition according to any of Claims 1 to 8 wherein the ethoxylated alcohol surfactant has the general formula:



wherein  $R_1$  is  $C_4-C_{31}$  hydrocarbyl, preferably  $C_6-C_{19}$  hydrocarbyl, more preferably  $C_7-C_{11}$  hydrocarbyl, most preferably  $C_9-C_{11}$  hydrocarbyl, including natural or synthetic materials having straight-chain, branched chain alkyl and /or alkenyl configuration,  $R_2$  is typically, hydrogen,  $C_1-C_8$  alkyl or hydroxyalkyl and  $x$  is an average value of ethoxylation ranging from 1 to about 20, preferably from about 3 to about 15, more preferably from about 5 to about 12, most preferably from about 7 to about 10

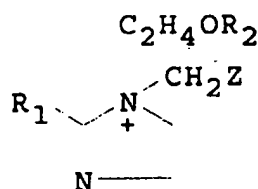
10. A composition according to Claim 9 wherein  $R_1$  is  $C_6-C_{19}$  hydrocarbyl,  $R_2$  is hydrogen and  $x$  is an average value of ethoxylation ranging from about 5 to about 12.
11. A composition according to any of Claims 1 to 10 wherein the ethoxylated alcohol is selected from  $C_9$  to  $C_{11}$  alcohols having an average degree of ethoxylation of about 6 and  $C_9$  to  $C_{11}$

alcohols having an average degree of ethoxylation of about 8 and mixtures thereof.

12. A composition according to any of Claims 1 to 11 wherein the ethoxylated alcohol present at a level of from about 0.5% to about 10%, preferably from about 1% to about 8%, more preferably from about 2% to about 6% by weight.
13. A composition according to any of Claims 1 to 12 wherein the weight ratio of short chain alkyl sulfate surfactant to alcohol ethoxylate surfactant is in the range of from about 10:1 to about 1:10, preferably from about 5:1 to about 1:5, more preferably from about 3:1 to about 1:3
14. A composition according to any of Claims 1 to 13 wherein the total level of auxiliary surfactant is from about 2% to about 30% preferably from about 3% to about 25%, more preferably from about 5% to about 20% by weight.
15. A composition according to any of Claims 1 to 14 wherein the auxiliary anionic surfactant is selected from alkyl sulfates other than short chain alkyl sulphates having a chain length of C<sub>10</sub> or less, ethoxylated alkyl sulfates, alkyl glyceryl ether sulfonates, methyl acyl taurates, fatty acyl glycines, alkyl ethoxy carboxylates, N-acyl glutamates, acyl isethionates, alkyl sulfosuccinates, alkyl ethoxy sulphosuccinates, alpha-sulfonated fatty acids, their salts and/or their esters, alkyl phosphate esters, ethoxylated alkyl phosphate esters, acyl sarcosinates and fatty acid/protein condensates, and mixtures thereof.
16. A composition according to Claim 15 wherein the auxiliary anionic surfactant is selected from ethoxylated alkyl sulfate, alkyl ethoxy carboxylate and mixtures thereof wherein each auxiliary anionic surfactant can be present at a level of from about 0.1% to about 20%, preferably from about 0.1% to about 15%, more preferably from about 2% to about 15% by weight.

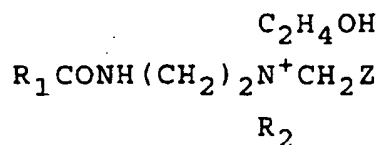
17. A composition according to any of Claims 1 to 16 comprising short chain alkyl sulfate and alkyl ethoxy sulfate anionic surfactants with ethoxylated alcohol nonionic surfactant wherein the short chain alkyl sulfate and alkyl ethoxy sulfate surfactant are present at a total combined level of from about 0.1% to about 30%, preferably from about 1% to about 20%, especially from about 3% to about 15% by weight.
18. A composition according to any of Claims 1 to 17 comprising short chain alkyl sulfate and auxiliary alkyl ethoxy sulfate anionic wherein the weight ratio of short chain alkyl sulfate to auxiliary alkyl ethoxy sulfate is in the range of from about 20:1 to about 1:20, preferably from about 10:1 to about 1:10, more preferably from about 5:1 to about 1:5, most preferably from about 3:1 to about 1:3.
19. A composition according to any of Claims 1 to 18 which additionally comprises from about 0.1% to about 15% by weight of auxiliary nonionic surfactant selected from C<sub>12</sub>-C<sub>14</sub> fatty acid mono- and di-ethanolamides, such as cocoethanolamide, cocomonoisopropylamide and ethoxylated derivatives thereof, polysachharide surfactants such as, C<sub>10</sub>-C<sub>18</sub> alkyl polyglycosides and polyhydroxy fatty acid amide surfactants.
20. A composition according to any of Claims 1 to 19 which additionally comprises an auxiliary amphoteric surfactant selected from:

(a) imidazolinium derivatives of formula [IV]



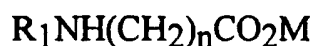
wherein R<sub>1</sub> is C<sub>7</sub>-C<sub>22</sub> alkyl or alkenyl, R<sub>2</sub> is hydrogen or CH<sub>2</sub>Z, each Z is independently CO<sub>2</sub> or CH<sub>2</sub> CO<sub>2</sub>M, and M is H, alkali

metal, alkaline earth metal, ammonium or alkanolammonium;  
and/or ammonium derivatives of formula [V]

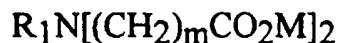


wherein R<sub>1</sub>, R<sub>2</sub> and Z are as defined above:

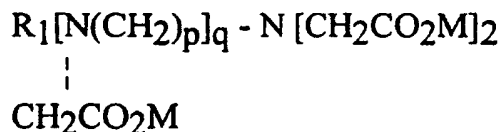
(b) aminoalkanoates of formula [VI]



iminodialkanoates of formula [VII]



and iminopolyalkanoates of formula (VIII)



wherein n, m, p, and q are numbers from 1 to 4, and R<sub>1</sub> and M are independently selected from the groups specified above; and

(c) mixtures thereof.

21. A composition according to any of Claims 1 to 20 comprising an additional auxiliary amphoteric surfactant selected from alkyl betaine, amido betaine, alkyl sultaine and mixtures thereof.
22. A composition according to any of Claims 1 to 21 comprising an additional optional cosmetic agent and /or pharmaceutical active at a level of from about 0.001% to about 10%, preferably from about 0.01% to about 5% , more preferably from about 0.1% to about 3%, most preferably from about 0.1% to about 2% by weight.

23. A composition according to any of Claims 1 to 22 wherein the additional optional cosmetic agent is a hair and /or skin conditioning agent selected from silicone materials, fatty alcohols, polymeric resins, polyol carboxylic acid esters, cationic polymers, insoluble oils and oil derived materials and mixtures thereof.
24. A composition according to any of Claims 1 to 23 comprising alkyl sulphate surfactant with alcohol ethoxylate and auxiliary surfactant, wherein no more than about 4%, preferably no more than about 2%, more preferably no more than about 1%, most preferably no more than about 0.5% by weight of the total composition comprises alkyl sulphate having a chain length of greater than 10 carbon atoms.
25. A method of making a shampoo composition according to any of Claims 1 to 24 wherein short chain alkyl sulphate is combined with ethoxylated alcohol and auxiliary surfactant and water.



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US97/12383 <b>(22) International Filing Date:</b> 16 July 1997 (16.07.97)  <b>(30) Priority Data:</b> 9615630.2                      25 July 1996 (25.07.96)                      GB  <b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> MCKELVEY, Graham, Neil [GB/GB]; 37 Raglan Road, Knaphill, Woking, Surrey GU21 1AR (GB). YOUNG, Wendy, Victoria, Jane [GB/GB]; 70 Edgell Road, Staines, Middlesex TW18 2EX (GB).  <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> BR, CN, JP, MX, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>  <b>(88) Date of publication of the international search report:</b> 14 May 1998 (14.05.98)
<b>(54) Title:</b> SHAMPOO COMPOSITIONS  <b>(57) Abstract</b>  A shampoo composition comprising: (a) from about 0.1 % to about 10 % by weight of short chain alkyl sulfate surfactant having a carbon chain length of 10 carbon atoms or less; (b) from about 0.1 % to about 10 % by weight of ethoxylated alcohol; and (c) from about 1 % to about 60 % by weight of auxiliary surfactant selected from anionic surfactant other than the short chain alkyl sulfate of (a), nonionic surfactant other than the ethoxylated alcohol of (b), amphoteric and cationic surfactants and mixtures thereof; (d) water. The shampoo compositions of the invention are valuable for the provision of improved rinsibility, excellent cleansing, and improved hair conditioning characteristics such as hair feel, hair shine, hair volume and manageability.		

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**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 A61K7/50

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A61K

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**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 671 895 A (ERILLI RITA ET AL) 9 June 1987 see the whole document ---	1,2,6-18
X	EP 0 554 943 A (UNILEVER NV ; UNILEVER PLC (GB)) 11 August 1993 see page 3, line 16 - page 6, line 19; claims 1-4,7 ---	1,2,6-21
Y	WO 93 15172 A (HENKEL CORP) 5 August 1993 see claims 1-11 ---	1-25
Y	WO 93 15172 A (HENKEL CORP) 5 August 1993 see claims 1-11 ---	1-25
X	EP 0 413 417 A (COLGATE PALMOLIVE CO) 20 February 1991 see page 4, line 46-47; claims 1-10; examples 8,13-15 --- -/--	1-8, 12-18, 22,23,25

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Date of the actual completion of the international search

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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 586 234 A (UNILEVER PLC ;UNILEVER NV (NL)) 9 March 1994  see the whole document  -----</p>	1-25

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/12383

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4671895 A	09-06-87	AT 396110 B	25-06-93
		AU 593851 B	22-02-90
		AU 6516586 A	21-05-87
		BE 905753 A	14-05-87
		BR 8605624 A	18-08-87
		CA 1285448 A	02-07-91
		CH 671026 A	31-07-89
		DE 3638314 A	21-05-87
		DK 547086 A,B,	16-05-87
		EG 17816 A	30-10-90
		EP 0228797 A	15-07-87
		FR 2590265 A	22-05-87
		GB 2182945 A,B	28-05-87
		HK 53493 A	11-06-93
		IE 59693 B	23-03-94
		JP 2527428 B	21-08-96
		JP 62143998 A	27-06-87
		LU 86661 A	26-06-87
		NL 8602896 A	01-06-87
		SE 467621 B	17-08-92
		SE 8604713 A	16-05-87
		TR 25922 A	01-11-93
EP 0554943 A	11-08-93	CA 2088230 A	04-08-93
		JP 5271690 A	19-10-93
		JP 8030199 B	27-03-96
WO 9315172 A	05-08-93	AU 3592993 A	01-09-93
		MX 9300608 A	01-09-93
		US 5403516 A	04-04-95
		ZM 493 A	25-05-94
EP 0413417 A	20-02-91	US 5051250 A	24-09-91
		US 4997641 A	05-03-91
		US 5213716 A	25-05-93
		AT 131034 T	15-12-95
		AT 118165 T	15-02-95
		AT 125689 T	15-08-95
		AU 5755890 A	03-01-91
		CA 2019341 A	21-12-90

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/12383

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0413417 A		CA 2019352 A	21-12-90
		CA 2019358 A	21-12-90
		CN 1048422 A	09-01-91
		DE 69016715 D	23-03-95
		DE 69016715 T	28-09-95
		DE 69021288 D	07-09-95
		DE 69023969 D	18-01-96
		EP 0407040 A	09-01-91
		EP 0407041 A	09-01-91
		EP 0413416 A	20-02-91
		EP 0407042 A	09-01-91
		GR 90100471 A	15-11-91
		JP 3051367 A	05-03-91
		US 5580494 A	03-12-96
		US 5348736 A	20-09-94
		US 5415857 A	16-05-95
		US 5346642 A	13-09-94
		AU 640382 B	26-08-93
		AU 5768890 A	16-05-91
		CA 2019346 A	21-12-90
		CN 1051501 A	22-05-91
		GR 1000728 B	23-11-92
		HU 210429 B	28-04-95
		JP 3153619 A	01-07-91
		NZ 234189 A	25-11-94
		PL 165297 B	30-12-94
		PT 94421 B	30-06-97
		TR 26442 A	15-03-95
		AU 635749 B	01-04-93
		AU 5755990 A	16-05-91
		CN 1051599 A	22-05-91
		GR 1000696 B	08-10-92
		HU 210123 B	28-02-95
		JP 3153620 A	01-07-91
		NZ 234190 A	26-08-94
		TR 26421 A	15-03-95
		AU 642651 B	28-10-93
		AU 5753390 A	10-10-91
		CN 1055481 A	23-10-91
		FI 97948 B	13-12-96

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/12383

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0413417 A		GR 1000710 B HU 209692 B	08-10-92 28-10-94
EP 0586234 A	09-03-94	AU 4603193 A CA 2105235 A CN 1090167 A JP 6157243 A	10-03-94 05-03-94 03-08-94 03-06-94